FT-IR SPECTROPHOTOMETRIC ANALYSIS OF IMPROVISED ORGANIC EXPLOSIVE FORMULATIONS

A
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By

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CERTIFICATE

This is to certify that this thesis **"FTIR SPECTROPHOTOMETRIC ANALYSIS OF IMPROVISED ORGANIC EXPLOSIVE FORMULATIONS"** embodies the work carried out by **Mr. Ashok Kumar Dalela, Junior Scientific Officer (Explosives),** himself under my supervision and that is worthy of consideration for the award of the Ph.D. degree.

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DECLARATION

I hereby affirm that the work presented in this thesis is exclusively my own and there are no collaborators. It does not contain any work for which a degree/ diploma has been awarded by any other University/Institution.

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Introduction

The abuse of explosives has always been there, since their discovery. A few decades ago, the bomb explosions were looked upon as unusual, but now these have become common events. Hundreds of explosions take place every year all over the world. In India alone, more than three hundred bomb explosions were reported per year in which thousands persons were injured or dead. Many of the famous Indian dignitaries like Mr. Rajeev Gandhi former Prime Minister of India and Mr. Beant Singh, then Chief Minister of Punjab, were assassinated during such explosions.

The abuse of explosives was comparatively rare in India before eighties. The types of explosive devices were also crude and not powerful. At that time commonly used explosives were pyrotechnic mixtures comprising inorganic salts. However, during the past two decades, the abuse of high explosives has increased tremendously, in India. The number of explosions and the power of the explosives used have gone very high, mainly due to the following factors:

Foreign Power(s)' Support:

Terrorists rocked Punjab for more than a decade. They are still devastating Jammu and Kashmir, courtesy Pakistan.

Political Ambitions:

Naxals in Andhra Pradesh, Bodos (and others) in the Eastern states of India and Maoists in the neighbourhood in Nepal are using explosives to create anarchy. Saddam Loyalists in Iraq are taking heavy toll (scores of persons are being exploded daily) in revenge. Their fallout also affects our country.

Organised Crime Syndicates:

The crime syndicates, like those Dawood Ibrahim, use explosives to further their financial, social and political ambitions. The impact of the Bombay blasts also during the year 1993 was very serious. The data of the loss of life and property is given as under:

- Dead   257

- Injured   713

- Property destroyed   Rs. 27 crore
  worth about
- Accused involved   204

- Time involved   The prosecution process, even after thirteen years, is still going on!

Sophistication in initiation:

Initiation of explosives has acquired so much sophistication that the explosive devices can be exploded through satellites from anywhere in the world and after any interval of time - from fraction of a second to months.

Massive destruction:

The explosives are not only the instruments of mass destruction but they also cause massive structural destruction. The explosives create so much debris in the process that most of the evidentiary clues are lost, making the task of investigating agencies to link the carnage with the culprit extremely difficult, if not impossible.

Easy availability:

Explosives are being manufactured and utilised by the armed forces. Explosives are also being used extensively in the construction of buildings, roads, dams and in mining operations for civil purposes. The explosives are smuggled out from these two sources by the bad elements for achieving their goals. Besides, the hostile neighbour countries are the ever ready sources for the supply of the latest type of explosives with all the paraphernalia required to carry out the nefarious tasks. They are transported by the notorious persons to the site of action in disguise.

Easy Improvisation:

Explosives can be created easily even from simple materials of daily use. For example cotton, ammonium nitrate and glycerine are common household items. It has been found that these items have been used to create explosives. However, as most of the terrorist organisations have connections in supporting foreign countries, thus, they are obtaining and

using powerful and task specific explosives. These explosives can be easily camouflaged and hence transported to the targets easily.

The manufacture of the explosives, in spite of its simple chemistry, is not everybody's cup of tea:

1. The manufacturing process is highly dangerous. A slight negligence or lack of knowledge on the part of manufacturer can literally explode him, the premises and other paraphernalia with a big bang. The big bang proclaims its perpetration too noisily to need any other evidence to identify the nefarious activity.

2. The manufacture of high explosives is governments' prorogation only. The explosive is manufactured under strict vigil of Govt. agencies. There are practically no cases of manufacture of high explosive clandestinely.

The explosives used by the terrorists and other criminals are therefore, smuggled either from the neighbouring countries or from the national production centres. In both the cases the explosives are usually smuggled in disguise to carry out nefarious tasks. The criminals have to adopt ever newer methods to avoid interception.

The manufacturing industries manipulate with the pure explosive substances for imparting typical properties of cast loading, stability, plasticity and desensitization. The extremists also do the same by adopting crude alternatives. No doubt, it reduces the lethality of the improvised

bombs matching to the quantity of the explosive substances used; however, the terrorists have been able to achieve reasonable success in destroying their targets. Viscous petroleum products, vegetable oils, fat and wax have been detected in explosive mixtures. Mixing of pure explosive substances with above materials facilitates shaping the charge suiting the containers of the improvised explosive devices. KHOYA – milk concentrate - can also act as a binder and a shaping agent. Wheat flour, Maida (refined wheat flour), Gram flour, Shakkar (brown sugar) etc., each on mixing in a suitable proportion with oil/ fat can also act as binder and plasticizer in a crude manner. Such mixtures of these crude binders with explosive substances will be easy to mould and shape so as to look like Indian sweets such as *BARFI, KALAKAND, PAIRHA, PINNI and MILKCAKE.* These manipulations can create near perfect deception of explosive formulations. It makes convenient the transportation of the explosive formulations by dodging Law-Enforcement agencies. In an attempt of a Jailbreak, wherein dreaded terrorists were lodged, guards seized sweet packets containing explosive substances moulded and wrapped with silver foil to look like PERHA. In another case explosive formulation moulded around a detonating cord looking like a garland was also seized. Sabotage of an Air India plane Kanishka above Atlantic Ocean using Improvised Explosive Device is still fresh in the minds of the people. Extremists anywhere in the

world conversant with Indian way of life can also adopt the tactics as they are practised in India, mentioned above.

The deception materials encountered belong to a wide variety of common substances of daily use, such as:-

1. Animal fats (butter, ghee, lard, tallow, etc.)

2. Vegetable oils, their blends, margarine etc.

3. Petroleum products especially diesel, heavy mineral oils, waxes etc.

4. Raw sugars (Shakkar, Gur, etc.)

5. Various types of flours.

6. Milk products like Khoya, Sweetmeats etc.

The explosive material used may be 2,4,6 – Trinitrotoluene (TNT), 2,4,6-trinitrophenylmethylnitramine (Tetryl or CE), Pentaerythritol Tetranitrate (PETN), 1,3,5-Trinitro-1,3,5- triazacyclohexane (cyclotrimethylene trinitramine or RDX), or any other explosive. Even a house hold item available to the criminals, is mixed with any of the above inert material and shaped into deceptive shapes and transported. The materials are useful as they serve as:

- Disguise materials

- Binders

- Modifiers, make them safer

It is true that the power of the explosive is reduced in the mixtures. However, this reduction is limited and is controlled by adding only such amount of the inert materials as not to reduce the power beyond the desired limits.

The governments of various affected countries are well aware of the smuggling and illegal transport of the explosives and explosive devices by terrorists and other criminals. But, at times, the men in the field find it difficult to recognise the explosives in their ever – changing disguise modes, with which the criminals are well aware. Thus, the Investigating Officers remain unaware with the transport of such explosive devices from one place to another. Although the governments are watchful of the possible trafficking of the explosives at the borders; or inside the country yet, they need assistance from the scientists to identify such suspicious consignment quickly and correctly whenever intercepted.

Routine methods of analysis of such mixtures in the laboratory may consume weeks together to achieve worthwhile results. It may forfeit the very aim of taking immediate preventive measures to safeguard the targets of extremists' activities. The aim of the present investigation is to develop a quick technique of analysis, which can provide immediate information of the composition of the explosive mixtures especially the explosive substance. There are a plenty of such substances already known and many others, which on mixing with, explosive substances can create disguise. It is

proposed to generate analytical data of a variety of substances comprising petroleum products, vegetable oils, fats, wax, starchy materials and sugars. Further, the mixtures containing these substances with frequently used explosive substances, in suitable proportions, will also be analysed to create their profile. The emphasis will be laid on correct confirmatory identification of explosive substances within minimum possible time.

Existing Technology:

The existence and the location of the explosives and explosive devices are best proved with the help of trained sniffer dogs. However, they do not provide information of a particular explosive for identification of explosive correctly; therefore the Investigation Officer has to depend upon the scientists for quick and correct identification. There is no dearth of methods to identify explosives. The common methods being used are:

1. **Colour tests**:

    Colour tests have been employed extensively for the detection of the presence of explosive substances. They have served well in the past but they may mislead in certain cases of some new explosives. The tests are not product specific and the class characterisation is also limited. Further, the material(s) used to disguise the explosive may mask the colour produced by reagents. All said and done, the colour tests are still useful preliminary tests.

2.   **Thin Layer Chromatography (TLC):**

Thin layer chromatography is an excellent workhorse in most of the analytical situations. It is used in the identification of the explosives. But, as in other techniques, it has its limitations:

- TLC is not product specific

- Certain impurities affect the mobility of the constituents,

- The Rf (Rate of Flow) values may be quite close to similar materials (homologues etc.).

- In cases of uncommon and unknown materials, a proper solvent(s) for mobile phase and the materials for stationery phase may have to be determined after extensive experimentation. The process may consume considerable time.

3.   **Instrumental methods:**

The instruments of choice, over the years, have been:

i.   Gas Chromatography (GC)

ii.   Liquid Chromatography (LC)

iii. Spectroscopy: Fourier Transform Infra Red (FTIR), Mass Spectrometry (MS), Nuclear Magnetic Resonance (NMR), Ion Mobility Spectrometry (IMS) etc.

iv.   Coupling of certain instruments like Gas Chromatograph- Mass Spectrometer(GC-MS),Liquid Chromatograph-Mass Spectrometer

(LC-MS), Gas Chromatograph- Thermal Energy Analyser (GC-TEA), Gas Chromatograph- Fourier Transform Infra Red Spectrophotometer (GC-FTIR).

These techniques have sensitivity of detection and identification of smallest of the small quantity; so much that particularly there is no amount too small for detection and identification.

Which technique should be used to analyse crude explosive formulations likely to contain explosive substances along with crude binders? The urgent demand from the methodology is that it should be capable and quick enough to tell about the identity of the substances comprising the mixture. There are some instruments like Gas Chromatograph, High Performance Liquid Chromatograph, Thermal Energy Analyzer, Ion Mobility Detector, Mass Spectrometer or Hyphenated techniques in which the sample introduced into the injector is made to reach the detector for its identification. The remnants of the crude mixtures of the explosives will adversely affect the performance of such instruments. No doubt these instruments can provide highly informative qualitative and quantitative results; however the samples will need plenty of time for their processing, to achieve such outputs. These mixtures as such may be even difficult to be flushed out completely from these instruments. On the other hand, Thin Layer Chromatography is devoid of above defects. Substances comprising crude mixtures can be identified tentatively by various

parameters including chromogenic reagents. However, substances comprising crude mixtures may contain many chemical compounds, thereby prompting to select numerous solvent systems for getting mere tentative results.

We could not locate, in literature, any convenient method already in use, nor could we find any data created on the lines which could be suitable for identification of the constituents of disguised explosives. The reason for lack was perhaps that the disguising of the explosives was probably unique to India only. It was, therefore proposed to select suitable method to meet the requirement of field workers and to generate data for the identification of the constituents (both active & inert) in the commonly used explosive mixtures. Zitrin (1) has recommended spectroscopic methods Infrared Spectroscopy (IR), Mass Spectroscopy (MS) and Nuclear Magnetic Resonance (NMR) Spectroscopy with the argument that the information obtained is more directly related to the molecular structures of the chemical substances. Infrared Spectrophotometry has been selected for the present study as it involves only preparation of a pellet of the sample with potassium bromide (KBr) and subsequently recording its spectrum. The technique has the capability of identifying the substances in the mixtures from many absorption peaks, which organics do generate in their spectra frequently. It is also proposed to generate analytical data in the form of IR spectra and typical absorption bands of a variety of substances comprising

petroleum products, vegetable oils, fats, wax, starchy materials and sugars. Further the mixtures containing these substances with frequently used explosive substances, in suitable proportions, will also be analysed to create their profile.

Analysis of post blast explosive residues:

Problem with identification of explosives from their residues left after blast has many facets. Pyrotechnic mixtures comprising inorganic substances lose their original identity and get transformed into many more salts. Ions common to such salt can also be present in the environment. Fortunately inorganic explosives and their mixture leave behind plenty transformed residues. Scientist has to search and evaluate experimental data for deriving at a correct conclusion. The moment organic and inorganic substances are involved; the scientist has to face the problem of availability of such materials in residues left after the blast. In properly initiated explosive bombs containing both organics and inorganics, organics are nearly destroyed and decomposed. Still certain inorganic converted to another salts due to blast conditions can provide link. Organic explosives containing both properties of oxidant and reducent on blast, simultaneously impart further complexity to identification due to their availability in traces and degradation & contamination.

Very common explosive substances TNT, CE, PETN and RDX are fully capable of blasting singularly on proper detonation. Extreme

conditions of blast leave behind only their trace amounts. Numerous degraded products can be generated due to the knocking of one or more nitro groups from their structures. Even ring structure can be opened, which may result in changing entirely their class of explosive substances. Of course, presence of contaminants in such samples after blast can be nearly undefined and unpredictable also.

Colour tests suffer from their inherent limits to deal with such trace contaminated organic explosive substances. High Performance Thin Layer Chromatography, Gas Chromatography and High Performance Liquid Chromatography can provide mere indication of their presence or absence (20). Thermo labile nature of explosive substances creates another problem of their degradation in Gas Chromatograph. Similarly Ion Mobility Spectrometer provides indirect inference regarding the nature of substance (20). Mass Spectrometer coupled with Gas Chromatograph / Liquid Chromatograph is the only suitable technique to solve the above problem (20). Even less than a microgram of sample can generate a spectrum indicating characteristic fragments with certain mass to charge ratios (m/z). Fragmentation generates a unique mass spectrum which entirely depends upon structural features of explosive substance. In spite of being a very potent technique to deal with such problem, instrumentation for Mass Spectrometer is very costly. It needs large infrastructure. Experimentation is very time consuming and also involves huge expenditure for maintenance.

In present study an attempt has been made with FTIR Spectrophotometry, to generate data of improvised organic explosive formulations, their constituent substances and post blast detection if possible, inspite of its requirement of a pure substance. Advancement of technology as a result of computer attachment was kept in mind to deal with the problem. FTIR spectrophotometer instrument itself is much cheaper as compared to Gas Chromatograph- Mass Spectrometer. Sample preparation is very simple. Moreover technique itself is non-destructive – an advantage over mass spectrometry. Experiments have been conducted with four substances TNT, CE, PETN and RDX. Strength of expanding of scale in x and y-axis and also the power of library software to detect characteristic absorption peaks representing particular organic structural moiety has also been examined.

Chapter-2

Review of Literature

Wide range of methods has been used for the identification of explosives. Variety of methods is now being used for quick identification of explosive substances at the spot. Many a methods are adopted in the laboratories as screening tests before conducting the final analysis for explosive substances or their formulations. In the recent past, a variety of methods and techniques have been tried with various degrees of success and a number of research publications dealing with explosives have appeared in various journals. These techniques are ranging from colour tests to highly sensitive techniques like Gas Chromatography- Mass Spectrometry.

Colour Tests:

Colour tests are handy and can easily be performed even by layman having little experience. Most of the explosives while undergoing colour tests, give specific colour with specific reagent. The colour reactions are not specific to a particular compound but they are specific to a group of compounds. The main disadvantage of colour tests for identification lies in their reliability, even though colour tests are extensively used as presumptive tests in many forensic and other explosive analyzing laboratories.

Some of the widely used colour tests described in the literature (2) according to classes of explosives are as follows:

The nitrate esters and nitramines were detected by the Griess procedure (3) using Sulphanilamide (8g. in 100 ml of 8% phosphoric acid) to form the diazonium cation and N-1-naphthylethylenediamine (0.4 g. of dihydrochloride salt in 100 ml of 8% phosphoric acid) as the coupling agent.

Di- and trinitroaromatic compounds develop colours with some basic solutions. TNT develops purple-brown colour whereas 2, 4-Dinitrotoluene and 2, 6- Dinitrotoluene develop yellowish colour when they react with alcoholic Potassium Hydroxide.

Another type of spot tests is based on the oxidation of a reagent by an explosive or an oxidizing constituent of an explosive mixture. Diphenylamine develops a blue colour when it reacts with triacetonetriperoxide (TATP); aniline sulphate develops a blue colour when reacted with chlorates.

Parker *et al.*(4) described various chemical tests for the identification of different explosives such as Greiss for nitrates, Nessler for ammonium, J-acid (4% solution of *6*-amino-1-naphthol sulphonic acid) test for RDX, and other tests for many cations and anions. These tests were developed by the Bureau of Alcohol, Tobacco and firearms (ATF) laboratories USA and have been found satisfactory.

Amas and Yellop(5) studied the reaction between RDX and Thymol in Sulphuric acid and devised a colour test which distinguished between RDX and 1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane(HMX).

Thin Layer Chromatography:

Thin Layer Chromatography (TLC) is the most widely used method for qualitative analysis of explosives and related compounds. It has the advantages of being simple, rapid, inexpensive and relatively sensitive (6 & 7). However, the combination of R*f* value and colour produced by spraying reagents used for detection are not considered sufficient for a final and independent identification of an explosive compound. This is because of the theoretical possibility that another compound would have same R*f* value and would also give the same colour. Even then, TLC serves as principal method for explosive analysis in many laboratories.

Douse (8) carried out analysis of eight explosives Ethylene Glycol Dinitrate (EGDN), Nitroglycerine (NG), TNT, PETN, RDX, Tetryl, HMX & Nitrocellulose (NC) on silica gel plates with a fluorescent indicator F_{254} using three developing solvents (A) toluene-cyclohexane (7:3), (B) chloroform-acetone (2:1) and (C) acetone-methanol (3:2). Out of these three solvent systems on which most of the explosives were well separated, toluene-cyclohexane (7:3) and for the separation of RDX & HMX, chloroform-acetone (2:1), were found most suitable. Acetone-methanol (3:2) was the only system which can elute NC. The nitrate esters and

nitramines were detected by spraying Greiss reagent (3). He also used 3, 3'-iminobispropyl-amine as spraying agent.

Koll *et al.* (9) separated TNT, PETN & RDX on aluminium oxide plates with petroleum ether-acetone (81:19) as developing solvent and located them by spraying with Potassium Hydroxide/Greiss reagent.

Baran (10) reported a scheme for the identification of military and mining explosives used in Poland, by TLC analysis. The military explosives included TNT, Tetryl, RDX, picric acid, hexyl (HMX) and PETN.

Hoffman and Byall (11) suggested a field kit which is capable of identifying black powder, smokeless powder, Dynamite, RDX, TNT etc.

Bagnato and Grasso (12) performed two dimensional TLC for the separation and identification of military & commercial explosives including picric acid, 2,4- dinitrophenol, HMX, RDX, o- & p-nitrotoluene, 2,4-DNT,TNT, Tetryl, Ethylene Glycol Dinitrate (EGDN), Nitroglycerine (NG), PETN and 1-nitronaphthlene, using solvent systems, light petroleum-dichloromethane; light petroleum-acetone; light petroleum-ethyl acetate; chloroform-acetone and light petroleum-benzene-acetone. Detection was achieved by 1% Diphenylamine in ethanol followed by UV irradiation.

Midkiff and Washington (13) used TLC as part of their post explosion analysis of military explosives and evaluated many previously reported TLC systems. According to them, RDX and HMX were best separated with chloroform-acetone (2:1) on silica gel plates to give R*f*.

values of 0.80 and 0.55 respectively, using visualizer Diphenylamine in ethanol followed by UV irradiation.

Parker *et al.* (14) separated acetone extracts of some organic explosives like DNT, Ethylene Glycol Dinitrate (EGDN), Nitroglycerine (NG), Nitrocellulose, RDX, PETN, Tetryl, and TNT by using silica gel G plates and chloroform as eluting solvent. Visualisation was achieved by 1% Diphenylamine in ethanol followed by UV irradiation (5-15minuts) and further spraying with concentrated Sulphuric acid.

Hass and Stork (15) used TLC to analyse soil and water samples contaminated with explosives, during World War II. The separation of TNT and some DNT isomers was carried out with light petroleum-ethyl acetate (85:15).

Jenkins and Yallop (16) used TLC on silica gel F_{254} plates for post explosion analysis using three developing solvents i.e. benzene for MNT, DNT,TNT, ethanol for NG and ammonium nitrate; and chloroform-acetone (1:1) for RDX, HMX, PETN and Tetryl. Nitrotoluenes were located by p-DMAB (dimethylaminobenzaldehyde). NG, NC, HMX, PETN and Tetryl were detected by Sodium Hydroxide /Griess reagent. Thymol/Sulphuric acid reagent was used for locating RDX and ammonium nitrate.

Helie-Calmet and Forestier (17) have written an extensive report on TLC examination of traces of explosives after detonation and also used two dimensional TLC systems.

Beveridge *et al.* (18) evaluated previously used TLC systems in order to analyse EGDN, NG, NC, PETN, RDX, DNT, TNT and inorganic nitrates. They found acetone-chloroform (1:1) on silica gel G plates, as most suitable system.

Verma *et al.* (19) of this laboratory applied TLC followed by examination under UV light and spray with chromogenic reagents for the tentative identification of organic explosives.

Gas Chromatography:

Gas Chromatography is a well established analytical technique for the analysis of volatile organic molecules. Widebore and nanobore capillary columns, which have now completely replaced packed columns, allow the separation of complex and contaminated explosive residues. The compatibility of Gas Chromatography with analysis of explosives is not self evident. Some explosives are too involatile to be analysed by Gas Chromatograph. The adsorption of highly polar explosive molecules on the stationary phase often affects their elution. The relatively high temperatures used during analysis could lead to thermal decomposition of heat labile explosives, especially nitrate esters or nitramines (20). However, controlled experimental conditions including the temperature of column and the injection port, the type and length of column and new injection techniques, have minimized some of the problems. Flame Ionisation Detector (FID) has

been more useful in the analysis of non-explosives carbon rich ingredients in explosive formulations, such as plasticizers, stabilizers and sugars (20).

Connor (21) suggested that Electron Capture Detector (ECD) is more sensitive for the compounds containing electronegative atoms such as halogen or nitrogen atoms, whereas it is less sensitive for hydrocarbons.

Kohler (22) analysed nitrotoluenes in ground water by capillary GC using FID detector. Analysis was performed on 12m X 0.2mm I.D. (Internal Diameter), OV-101 capillary column. The oven temperature was kept at 60°C for 1 min and then programmed to 150°C at 15°C/min. A splitless injection mode was used while maintaining injector & detector temperatures at 230 & 250°C respectively.

Keto (23) analysed the aliphatic oil fraction of the plastic explosive Semtex-H (containing RDX and PETN as main explosive ingredients) after extraction with hexane. The individual composition was not identified but overall GC profile was found to be similar to that obtained from 10W-40 multi-viscosity motor oil. Analysis was performed on 15m X 0.25mm I.D. (Internal Diameter), Quadrex high temperature capillary column. The oven temperature was programmed from 100°C to 350°C at 20°C/min. The injector and detector temperatures were maintained at 350°C.

Penton (24) used GC-ECD to analyse four common explosives, NG, TNT, PETN and RDX by on column injection. The separation was carried out on a 15m X 0.32mm I.D. (Internal Diameter) capillary column with SE-

30 stationary phase. On column temperature was 40°C initial temperature, programmed at 60°C/min to 160°C with a final hold of 9 min. The temperature was 60°C, programmed at 20°C/min to 160°C, with a final hold of 5 min.

Douse(25) carried out the GC-ECD analysis of industrial and military explosives EGDN, NG, TNT, RDX, Tetryl, HMX, 2,4-DNT, 2,3-DNT and 2,4-DNT with detection limits at low nanogram levels.

Hable *et al.* (26) studied the behaviour of RDX and HMX at the injection port of gas chromatograph. Several injection techniques were tried by them to check the thermal decomposition of these compounds.

Thermal Energy Analyzer (TEA):

Fine *et al.* (27) described the principal of operation of Thermal Energy Analyser for the trace analysis of volatile and non-volatile N-nitroso compounds.

Deak *et al.* (28) used Gas Chromatograph – Thermal Energy Analyser (GC-TEA) as a screening technique for the presence of common explosives in post blast exhibits. EGMN, EGDN, three MNT isomers, NG, 2,6-, 2,4-, 2,3- and 3,4-DNT isomers, TNT, PETN, RDX and Tetryl were analysed within 10 minute on 15m X 0.32 I.D. (Internal Diameter) DB-5 capillary column. The oven temperature was programmed from 50 to 170°C at a rate of 20°C/min and held at 170°C for 4 min.

Douse (29) suggested that peak broadening in capillary GC-TEA was electronic in nature. He modified the TEA detector and successfully used this detector in the analysis of NG, TNT and RDX.

Dionne et al. (30) used GC-TEA coupled to a vapour pressure generator for obtaining new data on the vapour pressures of RDX, PETN, TNT and NG. In this method a small amount of the explosive was used in equilibrium with a carrier gas, after filtration by a molecular sieve, passed through the explosive sample and exited, through a heated transfer line, to a cold trap (-78°C). The explosive vapours were washed from the trap with acetone and the washings were injected into a 30m megabore column with argon as carrier gas. The interface and pyrolyser temperatures were maintained at 280 and 900°C, respectively. The detection limits for these explosives were found between 30-50 picograms.

High Performance Liquid Chromatography:

High Performance Liquid Chromatography (HPLC) is considered to be the best technique for the analysis of thermo labile compounds. HPLC has been used for the detection and determination of explosive substances and their degradation products for almost 30 years. This technique is simple, reliable, accurate and precise. The technique provides a wide variety of separation modes and enables the separation and quantification of polar, non-polar and highly polar compounds without derivatization. It is a non-

destructive method. It can also be used in preparative mode for collection of desired fraction.

The initial history of explosive analysis by High Performance Liquid Chromatography suffered from a lack of selective and highly sensitive detectors. The detectors such as fixed wavelength Ultraviolet-Visible (UV-VIS) or Refractive Index (RI), used earlier were not selective. Now with the advent of new detectors like Diode array detector (PDA or DAD), variable wavelength UV-VIS detector, Electrochemical (EC) detector and above all Mass spectrometric (MS) detector, coupled with HPLC in the analysis of explosive substances has increased tremendously.

Parker *et al.* (31) separated TNT, RDX, Tetryl, PETN and Tetrytol (TNT and Tetryl mixed explosive) on two alternative columns: The RP-18 column with acetonitrile-water (50:50) used for the separation of RDX and Tetryl and RP-8 column with methanol-water (50:50) for separation of TNT, RDX and PETN. The UV detector wavelength was 254 nm.

Lyter (32) used HPLC for the separation of TNT, RDX, Tetryl, PETN, HMX, EGDN and NG. A reverse phase column was used, acetonitrile-water (70:30) was used as mobile phase at a flow rate of 1 ml/min and UV detector wavelength was fixed at 214 nm. All the seven explosives were separated within seven minutes. However, a low level of NG in presence of TNT or Tetryl or both was masked and could not be detected.

Anon (33) used a 3.3 cm Supelcosil LC-8 column for the separation of six explosives, TNT, RDX, Tetryl, HMX, 2,4-DNT and 2,6-DNT. Methanol with 2% tetrahydrofuran-water (30:70) was used as mobile phase at 2 ml/ min. flow rate. The UV detector wavelength was 214 nm. All the explosives were resolved in 3 minutes.

Keto (23) analysed the explosive ingredients of Semtex-H, (RDX and PETN) quantitatively by HPLC using a 10 cm X 8mm I.D. C-18 column (4μm particle size). Acetonitrile-water (70:30) was used as mobile phase at a flow rate of 1 ml/min and the UV detector wavelength was 210 nm.

Burrows *et al*. (34) separated RDX, HMX and the respective by-products from their synthesis, 1-acetylhexahydro-3, 5-dinitro-1, 3, 5-trizine (TAX) and 1-acetyloCtahydro-3, 5, 7-trinitro-1, 3, 5, 7- tetrazine (SEX), on a 25 cm X 4.6mm I.D. Zorbax C-8 column. The UV detector wavelength was fixed at 254 nm. Methanol-water was used as mobile phase at flow rate of 1.2 ml/min, having a linear gradient program with two solvent delivery systems. Pump 'A' contained methanol-water (1:4) and pump 'B' methanol-water (4:1); the methanol-water composition was changed from 'A'-'B' (95:5) to 'A'-'B' (50:50) in 25 minutes. The total separation time was 12 minutes.

Jenkins *et al*. (35) analyse major explosives and their potential interferences, in soil, on LC-18 and LC-CN (cyano) columns using water-methanol (50:50) for both the columns at a flow rate of 1.5ml/min.

De Bruyne *et al.* (36) analysed stabilizers and plasticizers of propellants by HPLC, using diode array detector. Separation was carried out on Chrompak C-8 column using acetonitrile water in various proportions.

Llyod (37) performed HPLC analysis of explosives using an Electro Chemical Detector (ECD) with a Pendent Mercury Drop Electrode (PMDE). The detection limits were 7pg for HMX and picric acid, 8pg for RDX, 9pg for TNT, 19pg for NG, 22pg for EGDN and 49pg for PETN.

Krull *et al.* (38) studied a series of explosives using HPLC- Electro Chemical Detector in the oxidative mode. The explosive compounds themselves can't be electrochemically oxidised because they are already in their highest oxidation state. The HPLC effluent was, therefore, irradiated post column with a UV lamp to form nitrate ions (NO_2^-) which could be detected at trace level by oxidative EC method. With dual electrodes, more qualitative and quantitative information was obtained. The separation was carried out on C-18 column. Methanol-0.1 M sodium chloride (50:50) was used as mobile phase at a flow rate of 0.6 ml/min. The electrodes were operated at +1.0 V and +0.9 V. The minimum detection limits of RDX, Tetryl and TNT were 25ppb.

Kurll and Bushee (39) have described the direct interfacing of HPLC with CG- Electro Chemical Detector, using the GC-ECD only as a vaporization oven and separated TNT, 2,4-DNT, EGDN, PETN and NG on a 25 cm X 4.6 mm I.D. Poliglosil 60-10N(CH$_3$)$_2$ column and detected by

ECD. Toluene was used as mobile phase at a flow rate of 0.85 ml/min. The detection limits at a signal -to- noise ratio of 3, were found to be 0.1ng for TNT and 2, 4-DNT, 0.5ng for RDX and 1.0ng for PETN.

Leffleur and Morriseau (40) demonstrated the HPLC analysis of a series of explosives- EGDN, PETN, NG, RDX, Nitroguanidine and HMX using a Thermal Energy Analyzer detector. The columns used were 25cm X 3.2 mm I.D. Lichrosorb Si-60 and 25cm X 3.2 mm I.D. Lichrosorb NH_2. Isooctane-ethanol was used as mobile phase at a flow rate of 1.5 ml/min. Thermal Energy Analyzer detector was operated at a pyrolyzer temperature of $550^{\circ}C$ with argon as the carrier gas at a flow rate of 25 ml/min and the reaction chamber pressure was maintained at 1.7 Torr.

Ultraviolet and Visible Spectroscopy:

Spectroscopic analytical techniques are based on the measurements of absorption of electromagnetic radiations.

In visible or ultraviolet (UV) spectroscopy, ground state electrons absorb incident radiations and rise to a higher energy excited state. The energy absorbed is measured as a function of frequency.

Amongst the organic explosives, nitroaromatics and nitramines show typical absorption bands in the UV or visible regions while nitrate esters do not absorb in these regions as mentioned by Yinon & Zitrin (3).

Schroeder *et al.* (41) studied the UV and Visible absorption spectra of 135 organic compounds including nitroaromatic compounds, nitramines and

nitrate esters, using ethanol as a solvent and observed a maximum at 213 nm for RDX.

Jones and Thorn (42) recorded the UV absorption spectra of 60 aliphatic nitrogen compounds as part of an investigation of the chemistry of RDX. The ultraviolet absorption spectrum of RDX was studied in ethanol, methanol, dioxane and water. It showed an inflexion near 240 nm instead of the maxima in the neighbourhood of 230 nm observed for most nitramines. The spectrum of HMX did not show this behaviour and the difference in shape of the curves of the two compounds was sufficient to allow the spectrophotometric assay of mixture of RDX and HMX.

The high sensitivity of UV absorption spectrometry made it susceptible to other compounds which absorbed in this region. Therefore, the method is limited to mixtures with known components only.

Ion Mobility Spectrometry:

Ion mobility spectrometer (IMS) consists of an atmospheric pressure ion source followed by an ion-molecule reactor attached to an ion-drift spectrometer (3). Sample ions formed in the reactor was injected into an electric field and separated according to their mobility as they travel through a drift gas. The ion mobility chromatogram or plasmagram consists of a plot of ion current as a function of drift time. The drift time depends on the ionic mass: the heavier ions move more slowly and therefore have longer drift time.

Spangler *et al.* (43) used Ion mobility spectrometer (IMS) to study the negative-ion mobility spectra of a series of explosives in ambient air. A dimethylsilicon membrane inlet was used on the IMS, to prevent entry of ambient water, ammonia, nitrogen oxides and halogenated compounds, while letting the sample pass. The purified air with water content of less than 4ppm was used as carrier as well as drift gases. The inlet temperature, drift-housing temperature and drift gas temperature were maintained at 227, 200 and 106-112°C, respectively. In composition B, contribution from DNT and TNT were observed, but not from RDX, probably because of its low volatility. The ion mobility spectrum of RDX was obtained by flash evaporating RDX dust deposited on a solid probe inserted through a special inlet into the ion source.

Huang *et al.* (44) used laser desorption to volatilize explosives for analysis by Ion mobility spectrometer/Mass Spectrometer (IMS/MS). The spectra were recorded in both air and pure nitrogen (as carrier gases) and were compared with those obtained by a direct in-beam heated probe. The ion source and drift tube were kept at 200°C. RDX produced $(M+NO_2)^-$ ion (m/z 268) with reduced mobility of $K_o=1.43$ $cm^2V^{-1}s^{-1}$. HMX, at a laser desorption temperature of 180°C, produced $(M+NO_2)^-$ and $(M+NO)^-$ ions.

Mass Spectrometry:

The detection and identification of explosives by mass spectrometry (MS) involves a wide array of interesting and challenging analytical

problems. As MS is a sensitive device for the trace quantities of material, it has become a routine technique for the detailed characterisation of various explosive and propellants.

In a mass spectrometer, the sample molecules are ionized and separated according to their mass to charge (m/z) ratio. The ions are detected and recorded, producing a mass spectrum. A mass spectrum often reflects the structure of a molecule. Identification of a compound is, therefore, highly reliable. In addition, mass spectrum can be used for structure elucidation of unknown compounds.

Introduction techniques include inlets for gases, liquids and direct insertion probe. However, the most common introduction techniques are the on-line combination with Gas Chromatograph i.e. GC-MS and High Performance Liquid Chromatograph i.e. LC-MS.

Various ionisation techniques available are Electron Ionisation (EI), Positive-Ion Chemical Ionisation (PCI), Negative- Ion Chemical Ionisation (NCI) and Atmospheric pressure ionisation (API). The separation of the ions formed in the source is carried by one of the several types of analyser. The most widely used analysers are the magnetic sector type and the quadrupole.

In the magnetic sector analysers, the ions are accelerated by a voltage of several Kilovolts and deflected by a magnetic field. The quadrupole analysers consist of four parallel rods to which an appropriate combination of DC and RF potentials are applied. Ions produced in ion source are

accelerated into the quadrupole field and filtered according to their m/z ratio.

Mass spectrometry is more suitable than IR spectrometry for post explosion analysis of explosives. The sensitivity is very important in post explosion analysis, where only small amounts of explosive are present.

Mass Spectrometry is probably the most suitable method for the identification of many organic components in trace quantities. In its usual mode- positive ions formed by Electron Ionisation (EI) - the mass spectrum of a pure compound is generally accepted as a proof of identity. Explosives from the same chemical class, such as nitrate esters, may have similar mass spectra in the EI mode but it is then possible to use Chemical Ionisation (CI) mass spectrometry. This technique compliments the EI mode by giving additional information, mainly in the molecular weight region. The combination of Electron Ionisation Mass Spectrometry (EIMS) and Chemical Ionisation Mass Spectrometry (CIMS) constitutes a very reliable method for a complete identification of most of the organic explosives (1).

Yinon and Zitrin (3) stated that the electron impact mass spectrometry of nitroaromatic compounds are characterized by loss of NO_2^- radicals, with retention of the charge on the aromatic nucleus. The alternative formation of NO_2^+ ion at m/z 46, which is the process in nitrate esters, is negligible in nitroaromatic compounds. Thus, EI mass spectra of 1, 3, 5-trinitrobenzene

(TNB) and 2, 4, 6-trinitrotolune (TNT) contain abundant $(M-3NO_2)^+$ ions at m/z 75 and 89 respectively, but only low abundant ions at m/z 46.

Another process in electron Ionisation mass spectrometry of nitroaromatic compounds is the loss of NO from the molecular ion to produce $(M-NO)^+$ ion, especially in compounds like picric acid, where the resulting $(M-NO)^+$ ions are stabilized by resonance. This ion does not appear in the EI mass spectrum of TNT. In TNT as in most of the nitroaromatic compounds, it is the complimentary process - formation of NO^+ ions at m/z 30 which predominates this process. The loss of NO must obviously involve some sort of rearrangement of the nitroaromatic $(ArNO_2)$ to an aromatic nitrite (ArONO).

As mentioned in "Forensic Applications of Mass Spectroscopy" by Yinon (45), out of the electron impact mass spectra of NG, TNT, PETN, EGDN and RDX, the nitrate esters NG, PETN and EGDN are characterized by only two ions m/z 46 $(NO_2)^+$ and 76 $(CH_2\text{-}O\text{-}NO_2)^+$. The molecular ions are never observed. So it is not a suitable technique for the analysis of nitrate esters.

Yinon (1) described that the EI spectra of RDX and HMX were very similar. In both spectra molecular ion can not be observed and the most abundant ions were $(NO_2)^+$ ion at m/z 46 and NO^+ ion at m/z 30. More diagnostic ions were at m/z 120, 128 and 148. Based on high resolution studies composition of ion at 120 was found $CH_2N (NO_2)_2^+$. He explained

the presence of two nitro groups in one CH_2N moiety as the precursor ion of the ion at m/z 120 was, at least partly, the adduct ion $(M+NO_2)^+$ at m/z 268, generally observed in CI mass spectra of nitrate esters and nitramines. Their appearance in the EI spectra of RDX and HMX is somewhat unusual, and could be the result of a high sample pressure in the ion source.

Yinon (46) studied the behaviour of TNT in both chemical ionisation (CI) and Negative chemical ionisation (NCI) modes. It was found that when using direct exposure chemical ionisation, i.e. bringing the sample very close to the electron beam, mass spectra of explosives could be obtained at lower temperatures and lower pressures than in normal CI. Mass spectra of TNT were thus obtained at source temperatures of 65-75°C and at an isobutane pressure of 0.08 Torr. The major ions were the MH^+ ion at 228 and the $(M-OH)^+$ ion at m/z 210, and a series of adduct ions $(M+C_3H_6)^+$ at m/z 269, $(M+C_3H_7)^+$ at m/z 270 and $(M+C_4H_8)^+$ at m/z 283. The $(M-OH)^+$ ion is the most abundant ion in the EI spectrum of TNT. Its presence in the CI spectrum could be attributed to EI processes occurring at a low isobutane pressure. Tetryl produces base peak of MH^+ at m/z 288 in CI isobutane mass spectrum at a source temperature of 65°C and source pressure of 0.09 Torr. RDX produces base peak at m/z 223(MH^+) with isobutane as reagent gas, at a source pressure of 0.15 Torr and a source temperature of 75°C. Under same conditions as of RDX spectrum of PETN was also recorded. An MH^+ ion at m/z 317 and some other abundant adduct ions were also

observed. The base peak at m/z 359 was attributed to $(M+C_3H_7)^+$, an adduct ion frequently observed in low pressure mass spectra with isobutane as a reagent gas.

Yinon (47) recorded the CI-water mass spectrum of a plastic explosive containing RDX and PETN which had been used in a '*letter bomb*'. The most abundant ions in the mass spectrum of RDX were observed at m/z 241 $(M+H_3O)^+$ and at 93 $(CH_2NNO_2+H_3O)^+$. Abundant ions were also observed at m/z 223 $(MH)^+$, 149 $[2(CH_2NNO_2)+H]^+$ and 75 $(CH_2NNO_2+H)^+$. A low abundant but typical ion in the CI-water mass spectrum of the mixtures was observed at m/z 539 due to the 'mixed dimer' ions $(M_{PETN}+M_{RDX}+H)^+$.

Gas Chromatography-Mass Spectrometry:

The powerful separation capabilities of Gas chromatograph, especially Capillary Column Gas Chromatograph, together with high reliability and sensitivity of Mass Spectrometer, have made GC-MS a leading method in the analytical organic Chemistry.

In modern GC-MS instruments, complex mixtures are separated by Capillary Column GC, and each of the separated compounds enters directly into the ion source of the mass spectrometer. This capability allows the rapid identification of every single component in a complex mixture, a task that in the past could take many years. In addition, to its principal role as identification tool, the mass spectrometer serves as a detector for the gas

chromatographic system.   It can measure the total ion current which is proportional to the concentration of the eluted component in the mixture. The resulting chromatogram, which is identical to a conventional GC trace, is termed as Total Ion Chromatogram (TIC) or Reconstructed Ion Chromatogram (RIC).

The use of GC-MS for the analysis of explosives (3, 48) is limited to those explosives which can be eluted from the GC column. Several explosives, especially some nitrate esters and nitramines, are thermally labile and could decompose under GC conditions. Others are too involatile to be analysed by GC.

The Electron Ionisation (EI) and Chemical Ionisation (CI) spectra of Tetryl obtained by GC-MS (49) were different from those obtained earlier by the solid probe method.   Recently it has been found that Tetryl decomposed completely to N-methylpicramide under GC conditions (50). Indeed, the EI and CI mass spectra of Tetryl obtained by GC-MS were found to be identical with those of N-methylpicramide.

Tamiri & Zitrin (50, 51) analysed six explosives (NG, 2, 4-DNT, TNT, PETN, RDX and Tetryl) by Gas Chromatography-Electron Ionisation Mass Spectrometry (GC-EIMS). The column used was 15m X 0.25mm I. D. DB-5 capillary column with a 0.25µm film thickness. The oven temperature was programmed from 70 to 270°C at 15°C/min. The injector temperature was 180°C. The MS conditions were electron energy 70 eV, ion source

temperature $140^{\circ}C$, scan range 40-500 u in the EI mode. All the six explosives were separated on a 15 m column. With a 30 m conventional column, RDX and PETN either failed to elute or showed partial thermal decomposition. The decreased resolution caused by the shorter column was not a major problem because in most of the GC-MS analysis of explosives, the GC served as a selective entrance to the MS rather than a separation device.

Yinon *et al*, (3 & 48) stated that many nitrate esters have very similar electron ionisation (EI) spectra. The electron ionisation (EI) mass spectra of NG, EGDN and PETN contain characteristic ions at m/z 30 (NO^+), 46 (NO_2^+) and 76 ($CH_2ONO_2^+$) but no molecular ion. This makes their identification by GC-MS extremely difficult.

Verma and Dalela (52) of this laboratory used very short capillary column (8 Feet) to reduce the degradation of explosives in long columns. They, after clean up of post blast residues by n-pentane, analysed five explosives TNT, CE, PETN, RDX and NG by GC-MS analysis.

Verma and Dalela (53) of this laboratory analysed five explosives NG, PETN, RDX, CE and TNT, using large volume programmable temperature Vaporising (LVPTV) Injector, (to get more residues available for detection) attached to Gas Chromatograph coupled with Electron Ionisation and Chemical Ionisation Mass Spectrometer (GC-EI and CI MS). The detection limits were found to be lower by Negative Ion

Chemical Ionisation (NICI) than by Electron Ionisation (EI) or Positive Ion Chemical Ionisation (PICI) for all explosives except RDX.

Cumming (54) carried out the Gas Chromatograph-Negative Chemical Ionisation Mass Spectrometry (GC-NCIMS) of explosives EGDN, NG, PETN, RDX and TNT using methane as a reagent gas and the resulting spectra were compared with their spectra obtained by GC-EIMS. The following detection limits were obtained in GC-NCIMS: EGDN 250 pg, NG 1ng, PETN 10ng, RDX 30 ng and TNT 125pg. The same values were obtained in GC-EIMS, except for TNT (50pg).

Sigman *et. al*. (55) determined detection limits and compared method for analysis of liquid injections of organic explosives and related compounds by gas chromatography-mass spectroscopy utilizing electron ionisation (EI), negative ion chemical ionization (NICI) and positive ion chemical ionization (PICI) detection methods. Detection limits were rigorously determined for a series of dinitrotoluenes, trinitrotoluene, two nitro ester explosives and one nitramine explosive. The detection limits are lower by NICI than by EI or PICI for all explosives examined, with the exception of RDX. The lowest detection limit for RDX was achieved in the PICI ionization mode. Judicious choice of the appropriate ionization mode can enhance selectivity and also significantly lower detection limits. Major ions are reported for each analyte in EI, PICI, and NICI detection modes.

GC-MS was found to be useful in the analysis of sugars after derivatization (56) with Tri-Sil-Z. The GC separation was carried out on 25 m X 0.2 mm I.D. HP-1 column with 0.25μm film thickness. The oven temperature was held at 140°C for 3 min and then programmed to 280°C at 8°C/min. Reducing sugars like fructose gave rise to multiple chromatographic peaks due to their tautomeric forms.

Reardon and Bender (57) analysed United States military Composition C-4 explosive, contains 91% cyclotrimethylenetrinitramine (RDX), 5.3% dioctyl sebacate or adipate (DOS or DOA), 2.1% polyisobutylene (PIB), and 1.6% oil. The original military specification required low viscosity engine oil but this has since been changed to a specially manufactured mineral oil which is also called "process oil". Differentiation of military and commercial Composition C-4 may be possible by analyzing the oil. In this study, samples of Composition C-4 were taken from various lots of U.S. military M112 demolition blocks from two commercially manufactured brands sold in the U.S. The oil and plasticizer were extracted with pentane and the plasticizer was removed using silica solid phase extraction cartridges. The oil was then analyzed by high-temperature gas chromatography/mass spectrometry (HTGC/MS). Results indicated that HTGC/MS is an excellent discriminating technique for oil comparisons.

Liquid Chromatography-Mass Spectrometry:

Liquid Chromatography is a powerful separation technique for the separation of organic molecules. It is equally suitable for the separation of polar and non-polar compounds. Thermo labile compounds like explosives can easily be analysed by this technique. The coupling of resolving power of high performance liquid chromatograph with the identification capability of mass spectrometry has resulted in a powerful analytical system.

Parker *et al.* (58) used on-line high performance liquid chromatography (HPLC)-negative ion chemical ionization (NICI) mass spectrometry for the analysis of explosive mixtures. The liquid chromatography-mass spectrometry (LC/MS) interface used was a commercial direct liquid introduction interface allowing about 1% of the solvent/sample effluent into the ion source. The HPLC mobile phases were acetonitrile: water (50:50) and methanol: water (50:50), which also served as NCI reagent gases. Standard mixtures containing 2, 4, 6-trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), Tetryl, & pentaerythritol tetranitrate (PETN) and a military explosive Tetrytol, have been analyzed by LC/MS system. The minimum detectable amount of TNT was 100 ng injected on column or approximately 1ng to the ion source.

Berberich *et al.* (59) investigated the application of liquid chromatography/thermospray/mass spectrometry (LC/TSP/MS) for the separation and identification of commercial and military explosives. The

analysis was performed using a reverse phase column with an isocratic mobile phase and a flow rate of 1.5 ml/min. These conditions, permitting rapid analysis, resulted in retention times of less than 3 min for common explosives. The thermospray was operated in the filament-on ionization mode which yielded unique spectra for the following explosive compounds: 1, 3, 5-trinitro1, 3, 5-triazacyclohexane (RDX), 1, 3, 5, 7-tetranitro-1, 3, 4, 7-tetrazacyclooctane (HMX), trinitrotoluene(TNT), dinitrotoluene (DNT), pentaerythritol tetranitrate (PETN), nitroglycerine (NG), diphenylamine (DPA), and monomethylaminenitrate (MMAN). The majority of explosives yielded only negative ion thermospray mass spectra, which exhibited a strong $[M+CH_3COO]^-$; however, components of double-based smokeless powders also yielded positive ion spectra. An important forensic science application of this work is the identification of commercial and military explosives. The Spectra obtained from the residues of improvised explosive devices of military C4 and a double-based smokeless powder allowed identification of the pure explosive compounds. Liquid chromatography/thermospray (filament-on)/mass spectrometry (LC/TSP (filament-on)/MS) provided limits of detection less than 2.5 picograms for PETN.

Xu *et al.* (60) developed a highly sensitive screening method based on high performance liquid chromatography atmospheric pressure ionization mass spectrometry (HPLC-API-MS) for the analysis of 21 nitroaromatic,

nitramines and nitrate ester explosives which include the explosives most commonly encountered in forensic science. Two atmospheric pressure ionization (API) methods; atmospheric pressure chemical ionization (APCI) & electrospray ionization (ESI) and various experimental conditions have been applied to allow the detection of all the 21 explosive compounds. The limit of detection (LOD) in the full-scan mode has been found to be 0.012–1.2 ng on column for the screening of most of the explosives investigated. For nitrobenzene, a LOD of 10 ng was found with the APCI method in the negative mode. Although the detection of nitrobenzene, 2-, 3-, and 4-nitrotoluene is hindered by the difficult ionization of these compounds, they have found that by forming adduct with glycine, LOD values in the range of 3–16 ng on column can be achieved. Compared with previous screening methods with thermospray ionization, the API method has distinct advantages including simplicity & stability of the method applied an extended screening range and a low detection limit for the explosives studied.

Voyksner and Yinon (61) used thermospray/liquid chromatography/ mass spectrometry (TS-LC-MS) in separation and identification of components of technical explosives without interference from plasticizers. They also detected explosives from hand swab with excellent sensitivity. They used both positive and negative chemical ionisation for the analysis of Semtex-H and found that positive ion detection was specific for the

plasticizers which eluted early from the column whereas negative ion detection was specific for the two explosive components RDX and PETN.

Gapeev and Yinon (62) demonstrated that electrospray mass spectrometry when used with spectral libraries becomes a useful method for rapid identification of inorganic oxidizers commonly present in commercial and improvised explosives. Electrospray ionization mass spectra (ESI-MSp) of oxidizers reveal a series of characteristic cluster ions. Such a set of cluster ions can be regarded as a "fingerprint" of a particular oxidizer. With the aid of a spectral library, tentative identification of inorganic oxidizer becomes automated and an easy-to-implement process. The oxidizer identity may be further confirmed by using tandem mass spectrometry (MS/MS). Because it is not necessary to separate the components before analysis, results become available in real time. Little sample consumption and the ease of sample preparation should also be noted. The methodology can be readily employed on various ESI-MS systems that are already in use in analytical laboratories.

Mathis and McCord (63) studied the negative ion electrospray ionization mass spectrometric (ESI-MS) detection of adducts of high explosives with chloride, formate, acetate, & nitrate and demonstrated the gas-phase interaction of neutral explosives with these anions. The relative intensities of the adduct species were determined to compare the competitive formation of the selected high explosives and anions. The

relative stability of the adduct species varies yielding preferential formation of certain anionic adducts with different high explosives. To exploit this effect, an isocratic high-performance liquid chromatography/ electrospray ionization mass spectrometric (HPLC)/ESI-MS method was developed and used for the simultaneous analysis of high explosives using two different techniques for the addition of the anionic additives; pre- and post-column. Their results show that the pre-column approach provides similar results with improved selectivity for specific explosives. This method provides a qualitative and quantitative approach for the analysis and identification of high explosives by detecting characteristic adduct species for each explosive.

Holmgren *et al.* (64) demonstrated a new LC-MS method for the determination and characterization of three groups of commonly used organic explosives (nitroaromatic compounds, cyclic nitro amines and nitrate esters). The method was developed using a porous graphitic carbon (PGC) (Hypercarb) column. Twenty-one different explosive-related compounds - including 2, 4, 6-trinitrotoluene, its by-products and its degradation products were chromatographically separated in a single analysis. This efficient separation facilitates the identification of the manufacturer of the explosive using the identified analytes as a fingerprint. A final, conclusive identification of the analytes can be obtained using LC-MS equipped with an atmospheric pressure chemical ionization (APCI)

interface. Solvent effects on chromatographic behaviour were investigated, as were the effects of solvent mixtures and mobile phase additives. The number and the relative positions of the nitro groups within analyte molecules influence their order of elution; these effects were investigated. The data thus generated can be interpreted to support a hypothesis concerning the retention mechanism of nitro-containing compounds when using pyrolyzer Gas Chromatograph (PGC). Limits of detection ranged from 0.5 to 41.2 ng. The new methodology described herein improves the sensitivity and selectivity of explosive detection. The effectiveness of the method is demonstrated by the analysis of soil samples containing explosive residues from test fields in Sweden and Afghanistan.

Tandem Mass Spectrometry (MS/MS):

Tandem mass spectrometry is based on the combination of two mass spectrometers in tandem, with a collision cell between them. The sample introduction into the ion source can be either a single compound or a mixture. The first mass analyser separates the ions produced in the source. A precursor ion is selected and forced into a collision cell. In this cell, the ion beam collides with an inert gas, such as helium, resulting in collision induced dissociation (CAD or CID) of the entering ions. The fragment ions (secondary ions) thus produced in the collision cell are mass analysed by second mass analyser. The secondary ion mass spectrum provides a 'fingerprint' of the precursor ion.

Yinon (65) analysed TNT, picric Acid, picramide and Tetryl by laboratory made tandem mass spectrometer consisting of two magnetic sector analyzers with a collision cell located between them. The sample was introduced by solid probe. The ion source temperature was 150-200°C. Major fragmentation pathways in TNT included loss OH and H_2O. The loss of OH which was due to an '*ortho*' effect was followed by an additional loss of OH and by NO_2. The loss of NO was observed only in picric acid & picramide which contain the strong electron-donating hydroxyl and amino groups respectively. Ions with an electron-donating group '*para*' to a nitro group enhance the loss of NO owing to resonance stabilization of the product ion.

McLluckey *et al.* (66) conducted an MS-MS collision induced dissociation (CID) study of a series of explosives including nitrate esters using a VG ZAB MIKE spectrometer. Nitrogen was used as the collision gas. The source temperature was estimated to be ~ 200°C. Isobutane was used as reagent gas in CI and as electron-energy moderator gas in NCI. The collision induced dissociation (CID) spectrum of the MH^+ ion of PETN with CI produced a major secondary ion NO_2^+ at m/z 46 and small secondary ions at m/z 76 & 30 corresponding to $CH_2ONO_2^+$ and NO^+ respectively. With NCI, the most abundant ion in the high mass region for both PETN and NG, was the $(M+NO_3)^-$ adduct ion. The collision induced dissociation (CID) mass spectrum of the $(M+NO_3)^-$ ion at m/z 289 in NG contained three

major secondary ions: NO_3^- at m/z 62,($NO_3)_2^-$ at m/z 124 and [$(M+NO_3)^-$ NO_3-$HNO_2]^-$ at m/z 180. The CID mass spectrum of the $(M+NO_3)^-$ ion at m/z 378 in PETN contained $(M+NO_3$-$O)^-$ at m/z 362, $(M+NO_3$-$HNO_3)^-$ at m/z 315 and also the ions $(NO_3)_2^-$ and NO_3^- as in the CID spectrum of NG.

Yinon *et al.* (67) conducted a collision induced dissociation (CID) study of mass spectral fragmentation pathways in RDX and HMX using EI, CI, and NCI. The source was operated at a temperature of 180-210°C and the solid probe which was used for sample introduction, was not heated separately. It was found that many ions in RDX and HMX originated from the fragmentation of the adduct ions $(M+NO)^+$ and $(M+NO_2)^+$ in EI and CI and $(M+NO)^-$ and $(M+NO_2)$- in NCI. The decomposition of the ions $(M+NO_2)^+$ and $(M+NO)^+$ lead to a simple interpretation of some of the ions present in the EI mass spectrum of RDX. In all the three modes of ionisation, the mass spectral fragmentation of both RDX and HMX included N-N bond fission and also ring fission accompanied by elimination of CH_2NNO_2 groups.

Yinon (68) analysed Semtex-H in CI with isobutane. The peaks at m/z 223 and 317 for MH^+ ions of RDX and PETN respectively were further confirmed by MS-MS CID of these ions.

Infrared Spectrophotometry:

An infrared (IR) radiation refers broadly to that part of electromagnetic spectrum which comes between the visible and microwave

regions (69).   It is subdivided into three regions: the near infrared region between 12,500 and 4000 cm^{-1}, the medium infrared region from 4000 to 650 cm^{-1} and the far infrared region extending from 650 to about 100 cm^{-1}. Silverstein and Webster (70) stated that even a very simple molecule can give an extremely complex spectrum.   One has to take advantage of this complexity when matching the spectrum of an unknown compound against that of an authentic sample. A peak to peak correlation is excellent evidence for identity. Any two compounds, except enantiomers, are unlikely to give exactly the same IR spectrum.

When a molecule absorbs radiation its energy increases. The increase in energy may be in the electronic, vibrational, or rotational energy of the molecule. Changes in the electronic energy involve large quanta. Changes in the vibrational energy involve smaller quanta and changes in the rotational energy involve quanta even smaller than those of vibrational energy.   If the radiation is in the medium infrared region, both the vibrational and rotational energies of the molecule will change. Thus, the infrared absorption spectra of molecules result from transitions between the vibrational and rotational energy levels.

There are two types of molecular vibrations: stretching and bending. A stretching vibration is a rhythmical movement along the bond axis such that the interatomic distance is increasing or decreasing. A bending vibration may consist of a change in bond angle between bonds with a

common atom with respect to the reminder of the molecule without movement of the atom in the group with respect to one another. For example, twisting, rocking and torsional vibrations involve in change in bond angles with reference to a set of coordinates arbitrarily set up within the molecule.

Only those vibrations that result in a rhythmical change in the dipole movement of the molecule are observed in the IR. Each atom has three degrees of freedom corresponding to the Cartesian coordinates (x, y and z) necessary to describe its position relative to other atoms in the molecule. A molecule of n atoms therefore has $3n$ degrees of freedom. For nonlinear molecules, three degrees of freedom describe rotation and three describe translation: the remaining $3n-6$ degrees of freedom are vibrational degrees of freedom or fundamental vibrations. Linear molecules have $3n-5$ vibrational degrees of freedom, for only two degrees of freedom are required to describe rotation. Fundamental vibrations involve no change in the centre of gravity of the molecule.

The theoretical number of fundamental vibrations (absorption frequencies) will seldom be observed because overtones and combination tones increase the number of bands, whereas other phenomena such as mentioned below reduce the number of bands:

1. Fundamental frequencies that fall outside the 4000-400 cm^{-1}.

2. Fundamental bands those are too weak to be observed.

3. Fundamental vibrations those are so close that they may coalesce.

4. The occurrence of a degenerate band from several absorptions of the same frequency in highly symmetrical molecules.

5. The failure of certain fundamental vibrations to appear in the IR because of lack of change in molecular dipole.

Assignment for stretching frequencies can be approximated by the application of Hook's law. In the application of law, two atoms and their connecting bond are treated as a simple harmonic oscillator composed of two masses joined by a spring. The equation derived from Hook's law, states the relationship between frequency of oscillation, atomic masses and the force constant of the bond.

$$\bar{v} = \frac{1}{2\pi c} \left[\frac{f}{(M_x M_y)/(M_x + M_y)} \right]^{\frac{1}{2}}$$

$\bar{v}$ = the vibrational frequency (cm^{-1})

c = velocity of light (cm/s)

f = force constant of bond (dyne/cm)

Mx and My = mass (g) of atom x and y, respectively.

The value of f is approximately 5×10^5 dyne/cm for single bond and approximately two and three times this value for double and triple bonds respectively. When interactions occur between fundamental vibrations and

overtones or combination tone vibrations, such interaction is known as 'Fermi resonance'.

Instrumentation:

The building blocks of an FTIR are very different from the predecessor, the double beam (diffraction) infrared spectrometer. In FTIR, it has the chain as given vide Figure-I below:

Sc → Interferometer → Sample → Det
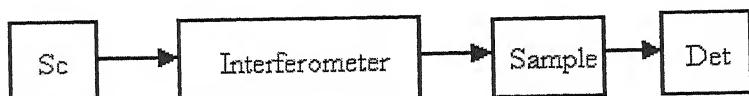
Source → Interferometer → Sample → Detector

Figure-I

Sources:

The Nernst Glower [a device utilizing the fact that some ceramics conduct electricity when heated. The Nernst had to be pre-heated and then could be used as a conductor and hence as a hot source].

Interferometers:

The interferometer is the heart of instrument. The interferometer is the bit that analyses the infrared or near infrared electromagnetic radiations and hence enables to generate a spectrum.

The classic Michelson Interferometer involves a beam splitter – a component which reflects about half of the radiation that hits it and transmits the rest. One bundle of radiation follows one path and the remainder a different path. The two bundles are then recombined and pass

out of the device. Now, one path is changed in length allowing radiation to interfere with that following the fixed path. In Figure 2, shows the classical diagram of the Michelson Interferometer.
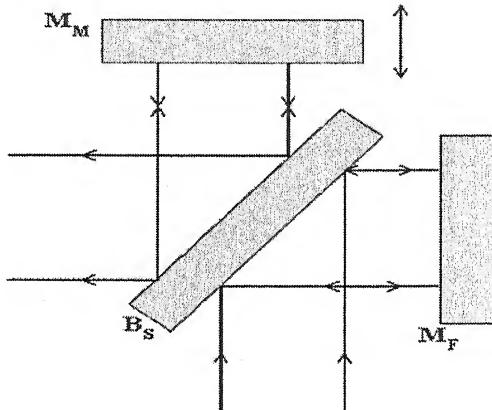
Figure-2

Parallel radiation entering the device hits beam splitter B_S and is either reflected to mirror M_F or transmitted to hit mirror M_M. Radiation reflected by the mirrors then passes either through or is reflected off the beam-splitter and hence either goes back towards the source or goes forward and out of the interferometer. Thus, only half the radiation entering the interferometer can get out in the OUT direction. Half of the radiation is reflected back towards the input.

Suppose monochromatic radiation of wavelength is λ. If the paths involving M_F and M_M are identical in length, about half of the radiation will pass through the interferometer, but if the paths differ by $\lambda/2$ when recombined on the beam-splitter, the two bundles of radiation will be out-of-phase and hence cancel each other out. Now, if M_M is moved, the

efficiency with which the interferometer will pass radiation follows what is shown in Figure-3.
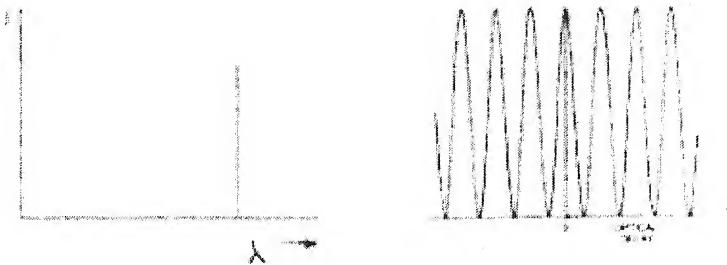
Figure -3

When the radiation of 2 wavelengths $\lambda 1$ and $\lambda 2$ is used, the result will be as shown below in Figure-4,
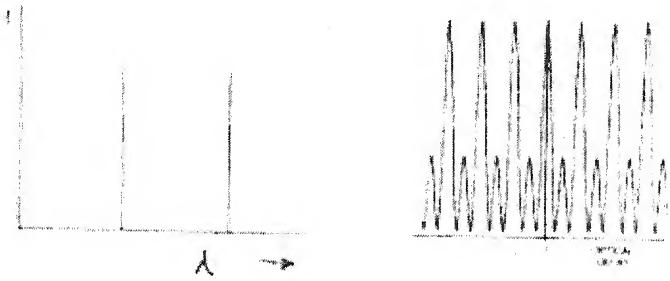
Figure-4

Sum of the two cosine functions is clearly observed from the above experiment. If white light is used, one will see the sum of all the cosine functions typical of ALL the wavelengths. Now, note one feature – at zero path difference all the radiation of whatever wavelength passes through the interferometer. At any other path difference, only some will pass. Hence, the plot of the efficiency of transmissions vs. path difference for white light looks something like

$\longrightarrow \upsilon$ or λ OPTICAL DELAY
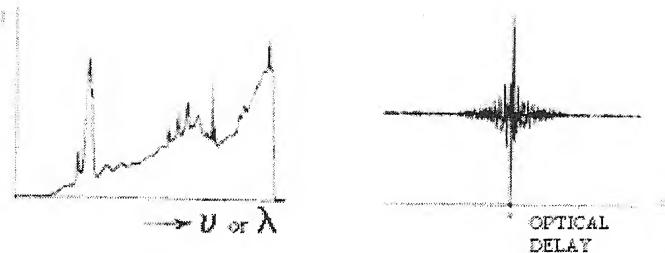
Detectors:

Peltier cooled Deuterated tri glycine sulphate (DTGS), the most common detector is generally used.

Practical use:

A complete IR spectrum of a pure organic explosive substance often constitutes reliable base for its identification. For organic molecules, the IR spectrum not only identifies functional groups by their characteristic absorption but often, due to its 'fingerprint' value, can identify the whole molecule. Even inorganic ions which appear in explosive mixtures have strong characteristic absorption in the IR region.

Organic explosive formulations are often mixtures of explosives with non explosive components. IR spectrometry can supply reliable information about the identity of the components in high concentration in simple mixtures. The spectrum of a compound known to present in the mixture can be artificially subtracted to enhance that of other component. This may reduce the need for chemical separation (2).

Yinon and Zitrin (3) stated that the symmetrical (v_s) and asymmetrical (v^+_{as}) stretching vibrations of the NO_2 group give rise to two strong absorption bands at wavelengths which depend on the type of atom to which nitro group is directly attached. These two stretching vibrations of NO_2 group have an important diagnostic value.

Raman evidence (71) indicates that in covalent nitrates, asymmetric and symmetric NO_2 frequencies are split farther apart and occur near 1640 cm^{-1} and 1260 cm^{-1}. Only a limited amount of information is available, but some results have been published on nitrocellulose (72) and on nitroglycerine (73, 74). Bellamy (75) stated that compounds such as isopropyl nitrate, EGDN, and PETN which contain this grouping and in these compounds, asymmetric frequency falls within the range 1650-1610 cm^{-1} and the symmetric frequency within the range 1300-1250 cm^{-1}. Brown (76) who has examined twenty-one nitrate esters has found characteristic stretching frequencies in the range 1639 ± 13 cm^{-1}.

Two NO stretching vibrations of $N-NO_2$ bond in nitramines were reported (77) to absorb in the range 1590-1530cm^{-1} and 1310-1270 cm^{-1} for asymmetric and symmetric vibrations respectively.

Glattstein *et al.* (78) used IR to measure RDX and PETN concentrations in plastic explosives used as letter bombs. Calibration was done by preparing a potassium bromide pellet with RDX and PETN with the addition of sodium azide as internal standard. Absorbance measurements

were done at 2140 cm^{-1}(Sodium Azide), at 790 cm^{-1} (RDX) and at 710 cm^{-1} (PETN). Absorption ratios at 2140 cm-1 to 790 cm-1 and at 2140 to 710 cm^{-1} were found to be linear over a wide RDX and PETN concentrations.

Elizabeth (79) developed a new method for determining the content of mixtures of 1,3,5,7-Tetranitro-1,3,5,7-tetrazocyclooctane (HMX) and 1,3,5-trinitro-1,3,5-triazocyclohexane (RDX), the HMX/RDX ratio, in explosive compositions by Fourier transform infrared spectroscopy (FT-IR), in the regions MIR (mid infrared) and NIR (near infrared) with reference values obtained by chromatographic analysis (HPLC). Plots of relative MIR (A917 / A783) or NIR absorbance values (A4412 / A4317) versus HMX/RDX ratio determined by HPLC analysis revealed good linear relationships.

Banu F. *et al.*(80) studied Fourier transform infrared spectroscopy (FT-IR) methods and common chemometric techniques [including discriminant analysis (DA), Mahalanobis distances, and Cooman plots] to classify various types of dietary supplement oils (DSO) and less expensive, common food oils. Rapid FT-IR methods were then developed to detect adulteration of DSO with select common food oils. Spectra of 14 types of DSO and 5 types of common food oils were collected with an FT-IR equipped with a ZnSe (Zinc Selenaid) attenuated total reflectance cell and a mercury cadmium telluride a detector. Classification of DSO and some common food oils was achieved successfully using FT-IR and

chemometrics. Select DSO were adulterated (2-20% v/v) with the common food oils that had the closest Mahalanobis distance to them in a Cooman plot based on the DA analysis; and data were also analyzed using a partial least-squares (PLS) method. The detection limit for the adulteration of DSO was 2% v/v. Standard curves to determine the adulterant concentration in DSO were also obtained using PLS with correlation coefficients of >0.9. The approach of using FT-IR in combination with chemometric analyses was successful in classifying oils and detecting adulteration of DSO.

Anonymous (81) characterized various vegetable oils by the use of FTIR Spectrophotometry.

Chapter-3

MATERIALS AND METHODS

INSTRUMENT:
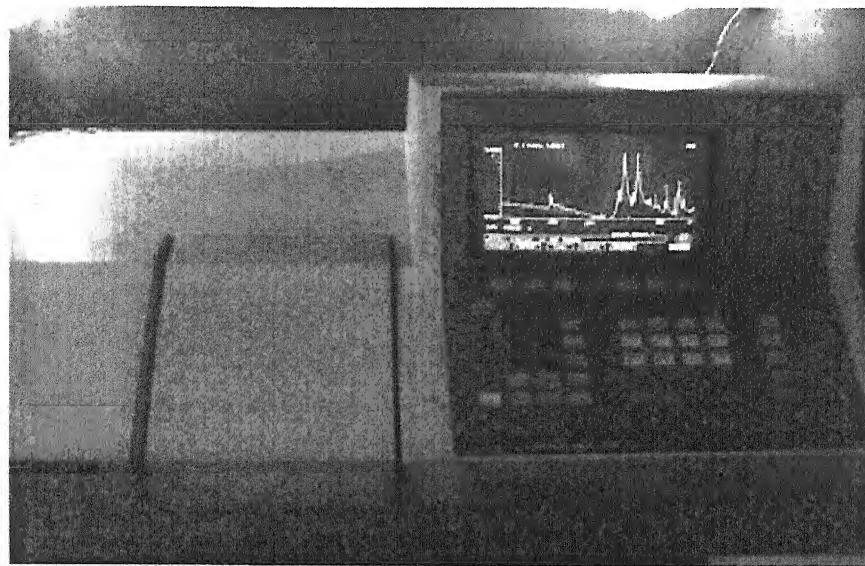
FT-IR spectrophotometer   Perkin Elmer   Model-1605:-

- Accumulations   :   4

- Detector   :   LiTA

- Resolution   :   4 cm-1

- Apodisation   :   Strong

- Spectrum Type   :   Magnitude

- Background Scan   :   4

- OPD Velocity   :   0.30 cm/sec.

- Igram Type   :   Double Sided

- Scan Direction   :   Bidirectional

- Zero Crossing   :   2

- IR Type   :   FT

- Accuracy Check   : $2850 \text{ cm}^{-1}, 1603 \text{cm}^{-1}, \& 906 \text{ cm}^{-1}$
  (Polystyrene Film)
  The Spectra were recorded through Perkin Elmer IR Data Manager.

Recorded spectra were processed by Perkin Elmer Spectrum 5.0.1 software.

The y-axis of all the spectra was extended by software to get good results.

MATERIALS:

i.   Potassium Bromide (Merck, Spectroscopic Grade)

ii.   Substances of petroleum, vegetable, animal, sugar and starch origin,

as detailed below:

a) Petroleum origin: High Speed Diesel (HSD), Liquid paraffin, Transformer oil, Multigrade gear oil (Castrol Hypoy 90), Engine oil (Castrol CRB Plus) Multigrade, Heavy duty engine oil (Servo Super Multigrade), (Two Stroke) 2T oil (Advance SX shell), (Two Stroke) 2T oil (Castrol Scootek), Used engine oil, Candle wax and Lubricating grease.

b) Vegetable Oils: Coconut oil, Sunflower oil, Cottonseed oil, Mustard oil, Rapeseed oil, Caster oil, Kardi & Corn blend (70% Corn + 30% Kardi) oil, Groundnut oil and Vegetable fat.

c) Animal Origin: Lard, Honey-bee wax, Milk fat and Milk Concentrate.

d) Sugars: Sugar, Shakkar (Brown sugar) and Gur (lumps of brown sugar)

e) Starch: Wheat flour, MAIDA (fine wheat flour) and Gram flour.

f) Explosive Substances: Trinitrotoluene (TNT), Tetryl (CE), Pentaerythritol tetranitrate (PETN), and 1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX). (Source: Terminal Ballistics Research Laboratory, Chandigarh, India).

g) Mixtures of explosive substances with oils, fat, sugars and starches.

h) Explosive exhibits received in the laboratory.

METHOD:

FT-IR Spectra of all individual substances in the range of $400cm^{-1}$ to $4000cm^{-1}$ of electromagnetic radiation were recorded using Potassium Bromide pellet method prepared by hand set dye. About 100 mg of spectroscopic grade dried Potassium Bromide stored in a desiccator, was used every time. Potassium bromide was pulverised using agate pestle mortar. About one milligram of the substance was also mixed and ground thoroughly. In case of liquid samples, a layer of the oil was made on Potassium bromide pellet. For mixtures, about 10% additive comprising oil or fat was thoroughly mixed with 90% of the explosive substance. This composition has been selected based on the past experience of working with such samples in the laboratory for quantitation of explosives in improvised formulations. Some samples, where substances like milk concentrate, starches and sugars mixed with explosive substance to produce a thick pasty formulation by adding oils, fat or wax, were also prepared. Quantities of the

explosive substances have been adjusted suitably, which can be 70% of the finished product.

3.1 Method for mixtures of explosive substances with oils, fat, sugars and starches:

Some of the well-known compositions, which contain wax and oil, are given in Table-1. Further, our experience of working with improvised explosive formulations indicated the presence of less than 10% oils or wax. Hence, mixtures of each of the explosive substances TNT, CE, PETN and RDX, with oils etc. were made by mixing explosive substance and the oil in a ratio of 90:10. Combinations were thoroughly ground to produce as much homogenous product as possible. About one milligram of the sample was pulverised with 100 milligrams of potassium bromide. The pellet prepared by manual die was further analysed with FT-IR Spectrophotometer.

TABLE-1

Name	Nature and amount of additives
Composition A-3	Wax 9%
Composition A-4	Wax 3%
Composition B	Wax 1%
HBX	Wax 4%
Prillex	HSD 6%
Lambrit	Fuel oil 6%

Spectra of four explosive substances mixed with different petroleum products were recorded and marked as g.1 to g.44, with vegetable oils as g.45 to g.80 and with lard, honeybee wax and milk fat as g.81 to g.92 respectively. Spectra of four explosive substances with milk concentrate in 1:1 ratio have been recorded and marked as g.93 to g.96. However, explosive substances with milk concentrate on mixing in a ratio of 3:1 also formed a mass, which can be moulded to desired shape. Spectra of the explosive substances with Indian sweets such as *BARFI, KALAKAND, PAIRHA, MILK CAKE and PINNI* were not recorded as explosive formulations are generally shaped to imitate these products. Further, these products mainly comprise milk concentrate/starch and sugar.

Some spectra were also recorded by mixing brown sugar and wheat flour with one of each of petroleum products, vegetable oils and milk fat separately and combining the same with each of the four explosive substances in such a way so that the final product could change to dough ($\cong 50\%$ explosive substance). No doubt, in such combinations explosive substance can be mixed up to 70% to form the dough. The reason for recording spectra of the dough with 50% concentration of the explosive substance is to explore the possibility to identify the explosive substances even up to this reduced concentration level. The spectra of combination of brown sugar with engine

oil, groundnut oil and milk fat with TNT, CE, PETN and RDX, were recorded and marked as g.97 to g.108. Similarly, spectra g.109 to g.120 represent combination of starch with HSD/ cottonseed oil/ lard with one each of the explosive substances TNT, CE, PETN and RDX respectively. Although, spectra g.1 to g.120 were recorded and marked but all of them have not been included in this thesis. Only spectra of those mixtures, which have been discussed in the following text, have been shown with marked figures at relevant places.

3.2 Method for Case Samples:

About one milligram of the suspect substance was pulverised with about one hundred milligram of potassium bromide and its pellet was prepared for recording spectrum. FT-IR Spectra of suspected substances in the range of $400cm^{-1}$ to $4500cm^{-1}$ of electromagnetic radiation were recorded. Library match was carried out for the identification of the explosive substance. All absorption peaks in the spectra of the mixtures were scanned to get an indication of the modifying agents mixed with the explosive substances for moulding into desired shapes.

3.3 Method for Post Blast Samples:

First of all spectra of standard samples of organic explosives was recorded by mixing one mg of sample with 100 mg of Potassium bromide. Mixture was pulverized and pellet was prepared with handset die. Air was removed by applying vacuum to prepare a transparent pellet. Further

dilution of the sample was carried out with Potassium bromide and its spectrum was recorded. For each explosive substance on its dilution with Potassium bromide, a stage could be reached at which no characteristic peak could be seen. Spectrum was evaluated interse with respect to spectrum of the substance in 1:100 ratios with Potassium bromide. Based on characteristic peaks of each substance, minimum detectable limit was measured. Another attempt was made thereby decreasing amount of substance in Potassium bromide and then studying by expanded X-axis range. It was further explored to find out the effect of expanding y-axis i.e. absorbance. Thus three pronged attack was made to study minimum detection limit of each substance.

Case sample comprising exploded articles suspected to retain explosive residues were chosen. Preliminary analysis of such samples was carried out using Thin Layer Chromatography (TLC). The samples with positive indication of organic explosive substance were treated suitably with spectroscopic grade n-pentane. On removal of solvent vapours by air drying, the article was treated with acetone to dissolve explosive substance. A known volume of acetone extract was mixed with Potassium bromide to form pellet. Similarly soil sample lifted from blast craters were extracted and their FTIR spectra were recorded.

Identification of explosive substances available in trace amount in blast residues will be problematic due to the appearance of very small

absorbance bands alongwith a shift in wave number also. To reduce this problem and to enhance detection limits, it was proposed to record spectrum of a case sample and spectrum of the standard of likely substance simultaneously under identical conditions.

Chapter-4

RESULTS & DISCUSSIONS

The present study deals with the identification of four explosive substances namely; TNT, CE, PETN & RDX in their formulations. The four explosive substances are frequently used for disruptive criminal activity. Generally, criminals have the access to rather pure materials, which are mixed with moulding agents to impart proper shape suiting to the design of improvised explosive device. It is the proper shape of moulded formulation, which ultimately ensures desired results. The same can be seen in factory made bombs, guided bombs and missiles. It has been highlighted in the introduction that criminals go for easily available moulding agents, which have been found to be generally oils or fats of petroleum, plant and animal origin or starches and sugars in their combination. It assists in shaping the explosive substance to look like our daily household item such as sweets or dough. Presence of apparent common oil or fat does not produce suspicion but deception. Hence, different materials taken for their study in the present work have been classified into a group based on their similar chemical nature. Their recorded spectra have been studied carefully and minutely. Effort has been made to characterize strong absorption bands which can be used to detect individual material in formulations. Thus, each spectrum of individual substance forming a class of oils of petroleum

origin, oils and fats of plant and animal origin, sugars, starches, milk products, individual explosive substance TNT, CE, PETN & RDX, simulated samples formed by mixing explosive substances and moulding agents in a suitable proportion as found in criminal cases, have been studied as described below. Actual explosive organic formulations referred to the laboratory and even post blast samples of cases of national importance have also been studied to determine the success of the methodology and the scientific technique.

(a)   **Spectra of petroleum products**

All these substances comprise mostly of long chain hydrocarbons called paraffins. Absorption peaks (cm^{-1}) characteristic to the chemical structures of the compounds comprising the petroleum oils, wax and grease have been observed (81, 82, 83 & 84) in their spectra, as stated in Table-2.

TABLE-2

Peak (cm^{-1})	Group	Type of Vibration
2955 ± 1	$v_{as}CH_3$	Methyl Antisymmetric stretching
2924 ± 2	$v_{as}CH_2$	Methylene Antisymmetric stretching

2854 ±3	$\nu_s CH_2$	Methylene symmetric stretching
1460-1465	δCH_2	Methylene scissoring
1459	$\delta_{as} CH_3$	Methyl Antisymmetric bending
1377	$\delta_s CH_3$	Methyl symmetric bending (Scissoring)
1302-1305	ωCH_2	Methylene Wagging
1155-1166	τCH_2	Methylene Twisting
722	ρCH_2	Methylene Rocking

Spectra of eleven substances in the region 400 cm^{-1} to 4000 cm^{-1} of electromagnetic radiation are as shown in figure a.1 to a.11. Typical spectra of candle wax and grease can be seen in figures a.10 and a.11 respectively.
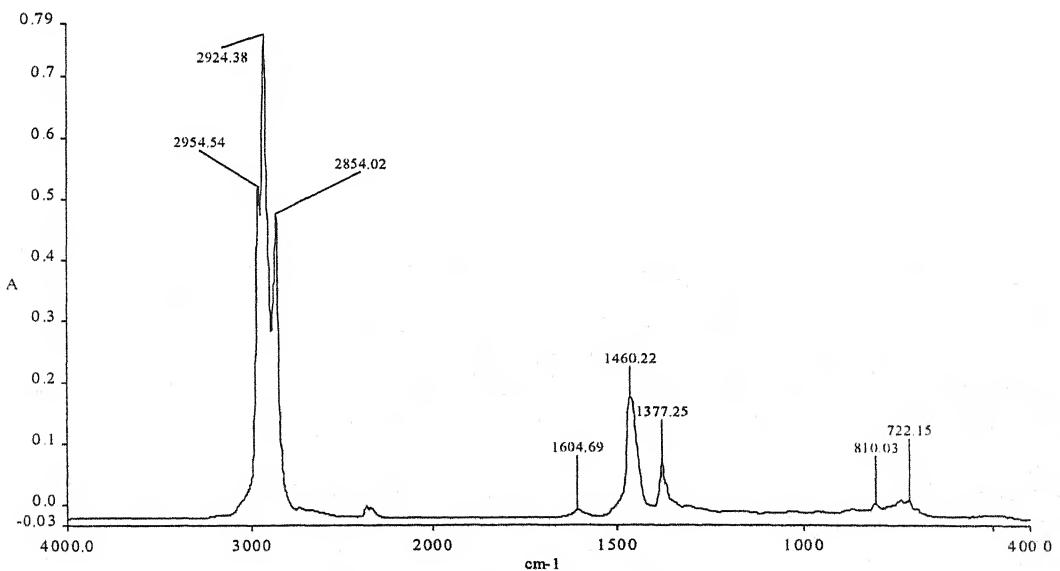
Fig.a.1-High Speed Diesel
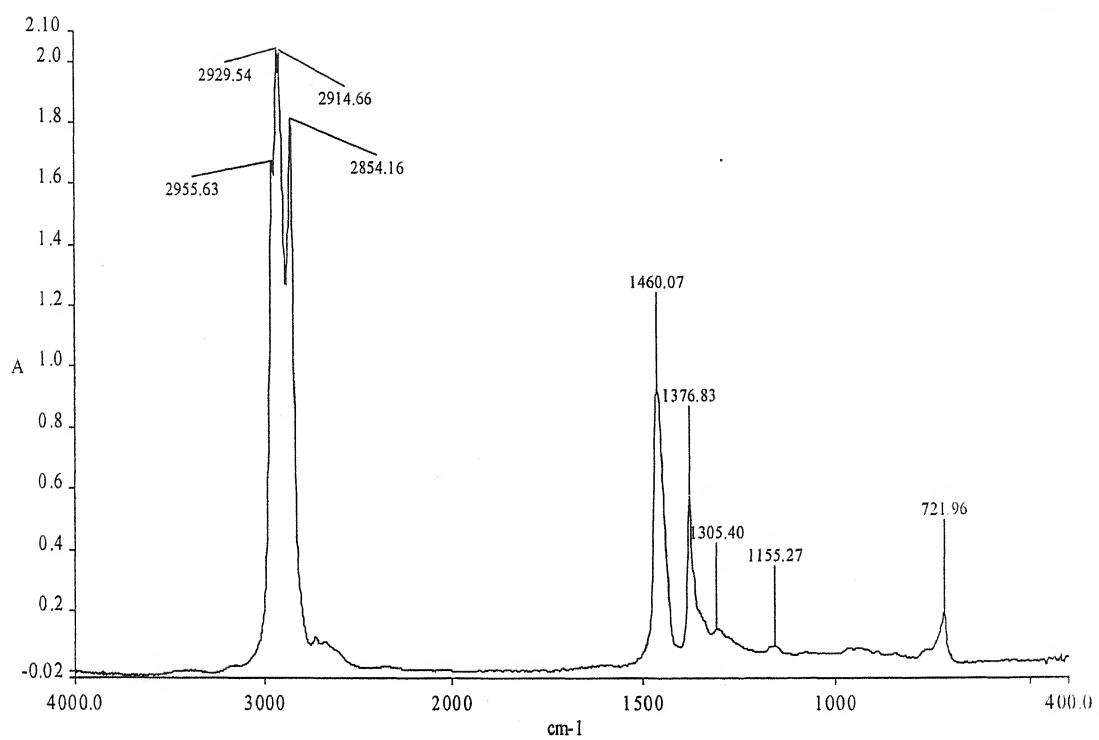
Fig.a.2-Liquid Paraffin (Oil)

Fig.a.3-Transformer Oil

Fig.a.2-Liquid Paraffin (Oil)

Peaks: 2955.63, 2929.54, 2914.66, 2854.16, 1460.07, 1376.83, 1305.40, 1155.27, 721.96

Fig.a.3-Transformer Oil

Peaks: 2931.84, 2922.06, 2855.62, 2727.89, 1461.22, 1376.96, 1305.61, 1156.35, 1004.44, 815.02, 722.23, 670.10
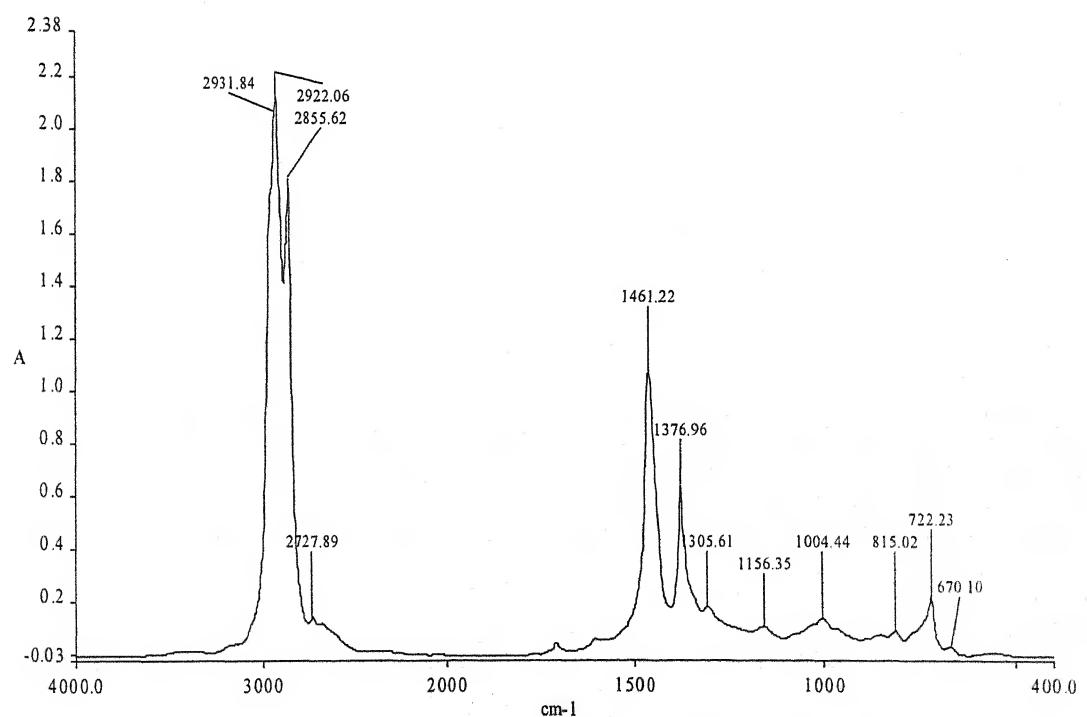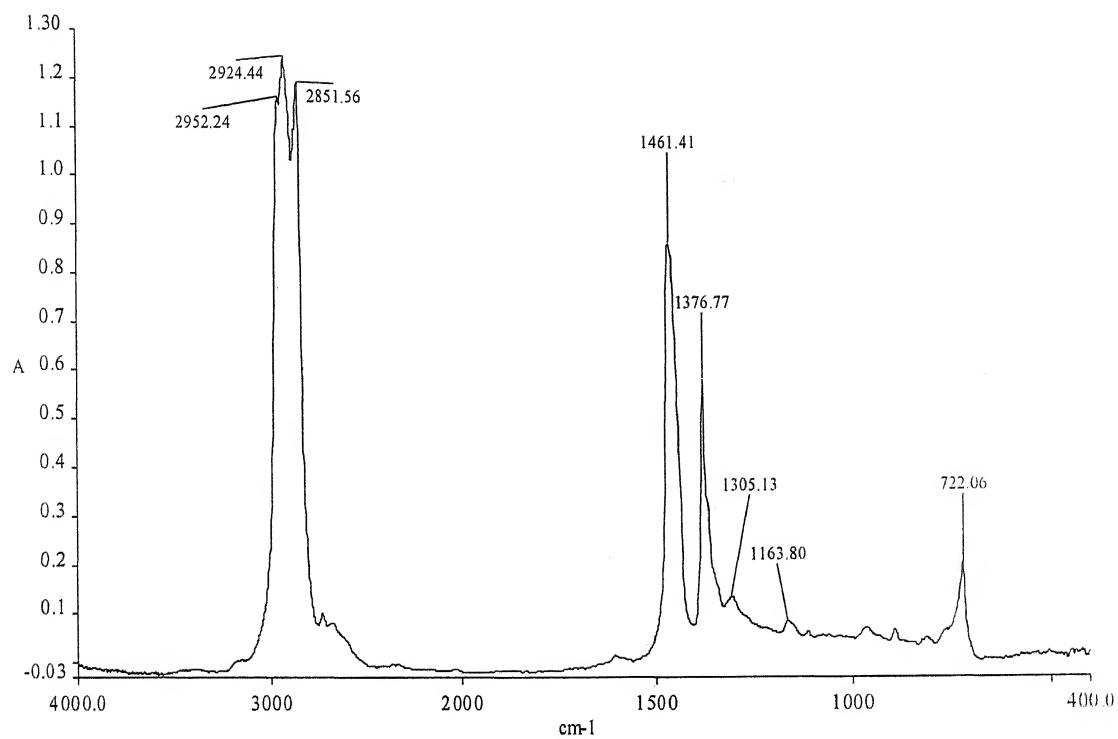
Fig.a.4-Gear Oil
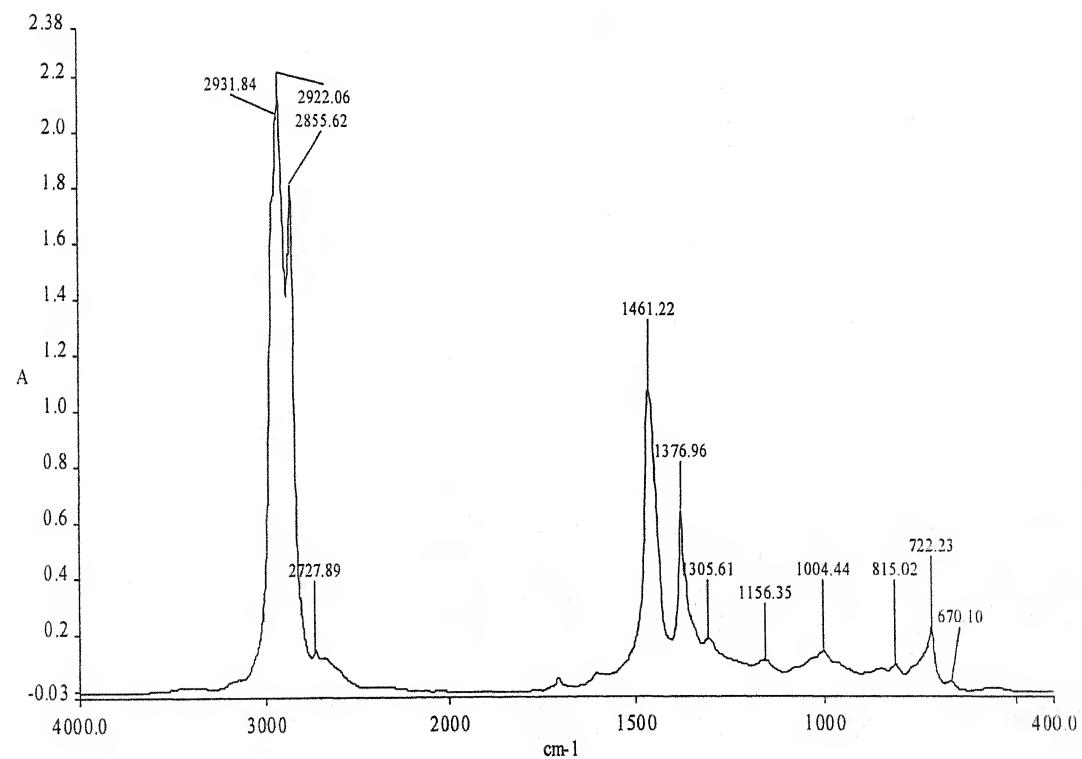
Fig.a.5-Engine Oil
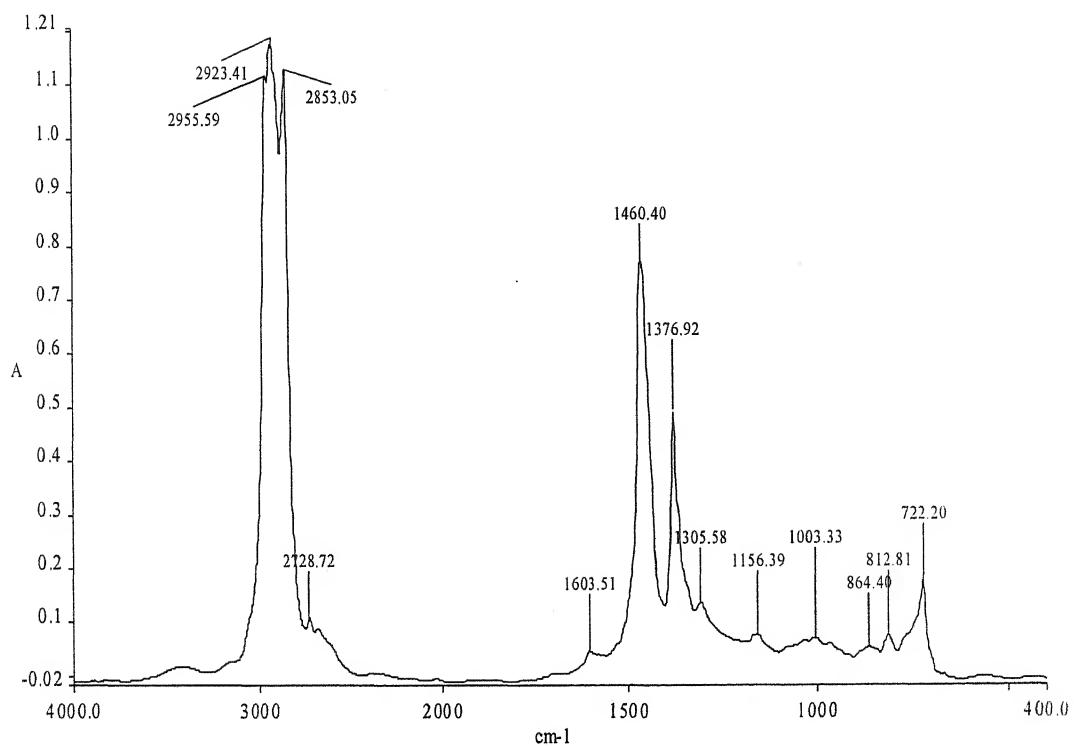
Fig.a.6-Heavyduty Engine Oil
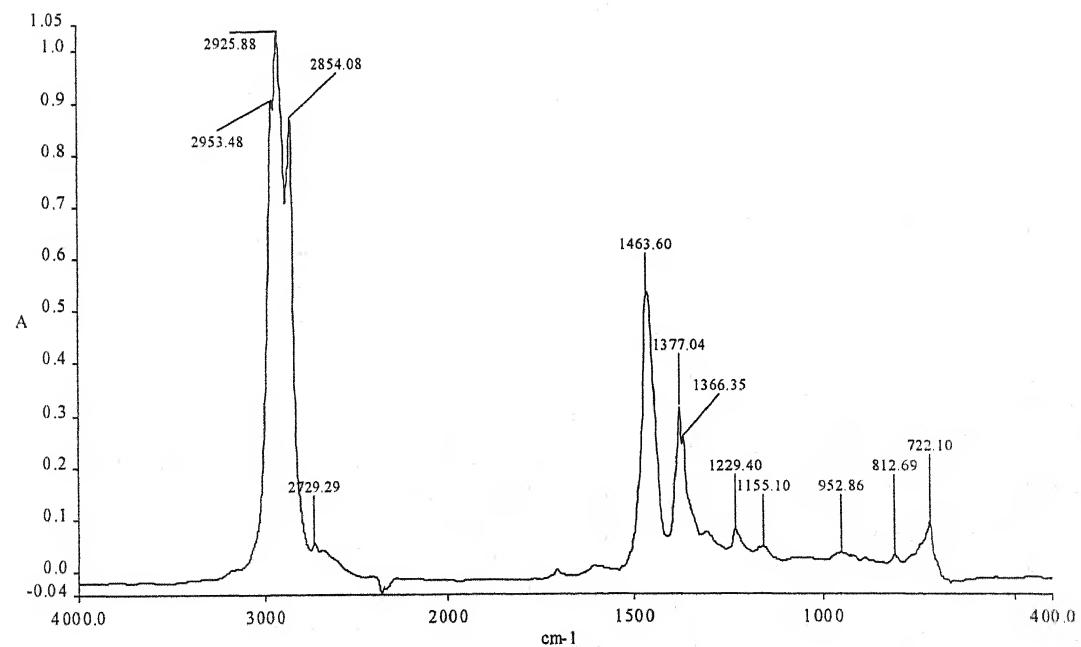
Fig.a.7-Shell 2T Oil
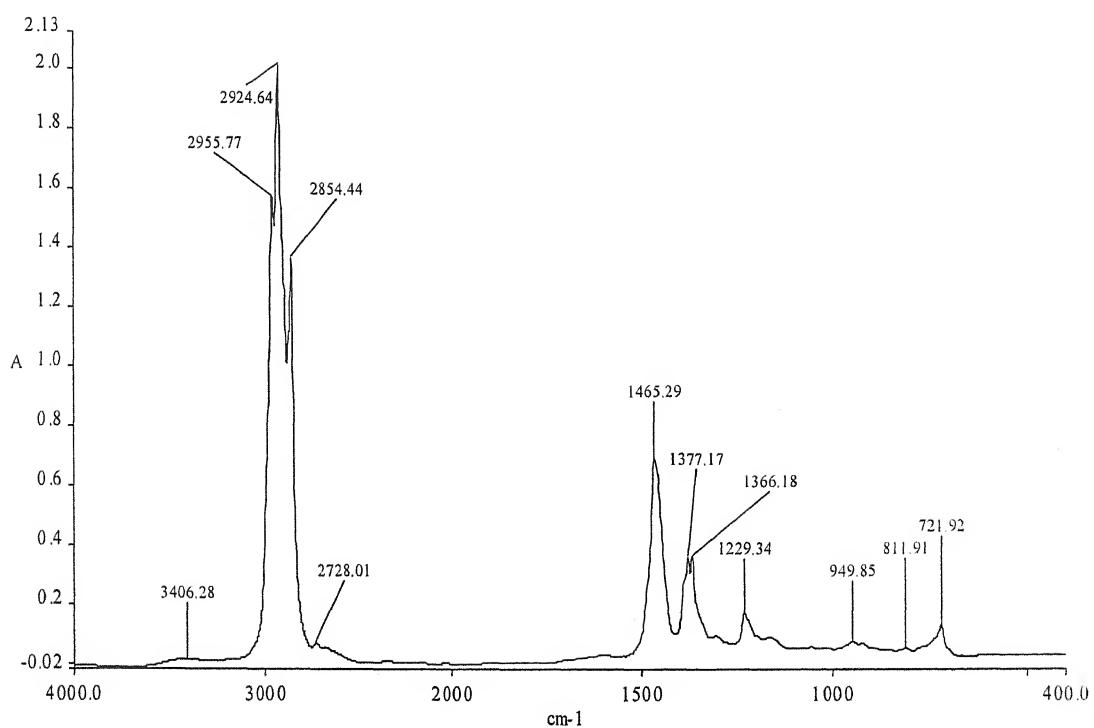
Fig.a.8-Castrol 2T Oil
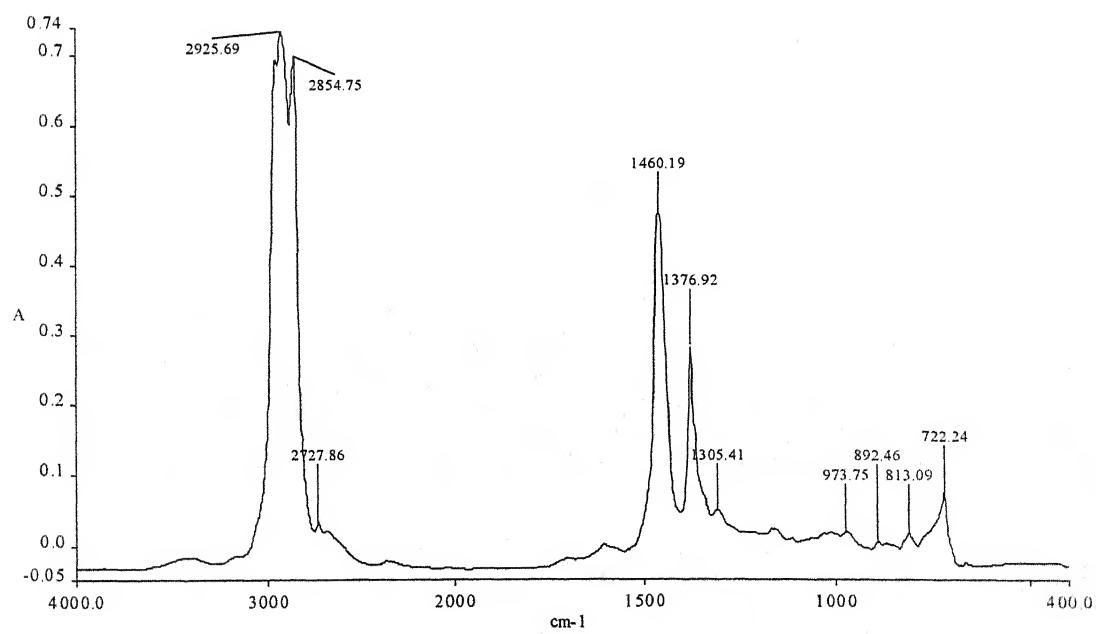
Fig.a.9-Used Engine Oil
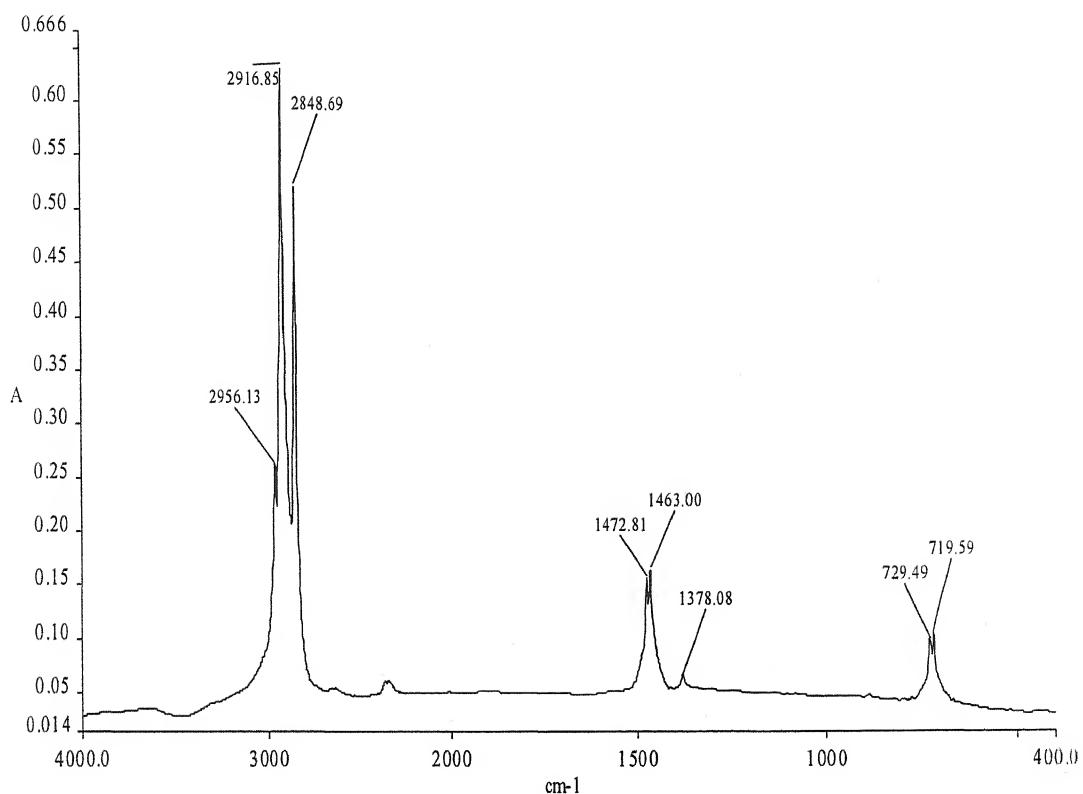
Fig.a.10-Candlewax
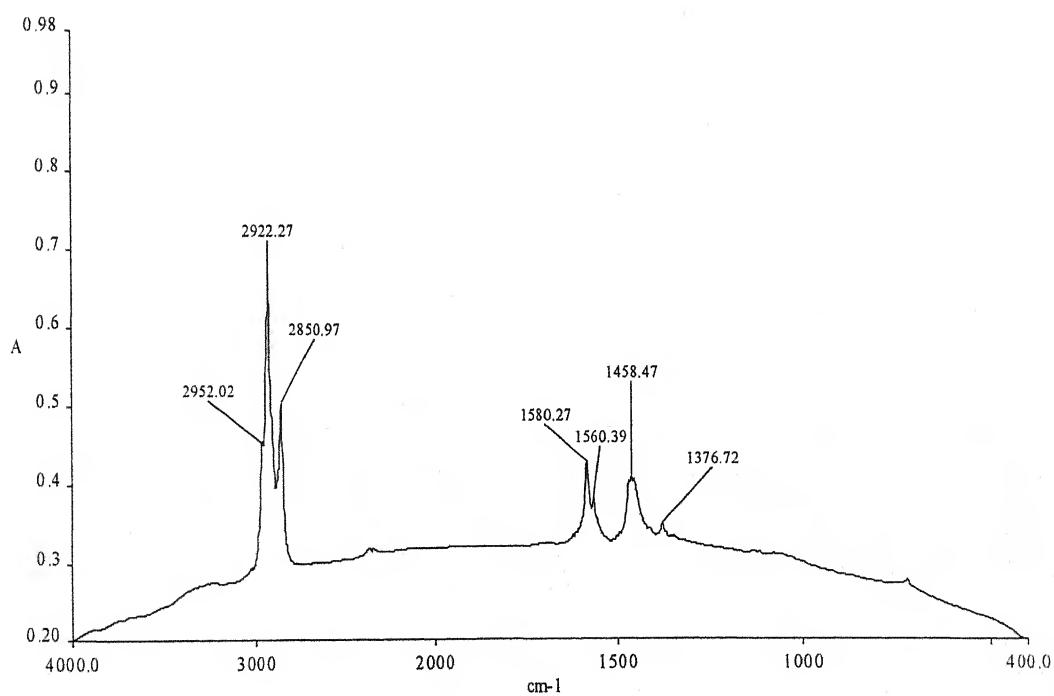
Fig.a.11-Lubricating Grease

Absorption peaks due to Methyl symmetric stretching ($\nu_s CH_3$ 2872 cm^{-1}), Methylene Wagging (ωCH_2 1302-1305 cm^{-1}), Methylene twisting (τ CH$_2$ 1155-1166 cm^{-1}) and some peaks representing aromatic character have been either obscured by neighbouring strong absorption bands or show insignificant absorption.

(b) **Spectra of Vegetable oils / fats**

All such oils of plant origin comprise esters (triglycerides) of numerous saturated and unsaturated long chain fatty acids. Unsaturation is caused by carbon-carbon double bonds, which can be even more than one in a chain of each fatty acid contained in these oils or fats. Spectrum of castor oil differs from the spectra of other oils and fats with respect to absorption peak at 3416 cm^{-1} which is due to the presence of secondary alcoholic group present in the ricinoleic acid, comprising 85-90% castor oil. Infrared spectrum of each of the other vegetable oils does not indicate any characteristic peaks to distinguish among one another except in the case of castor oil due to aforesaid reason. Prominent peaks (cm^{-1}) in the Infrared spectra of these nine substances are given in Table-3.

TABLE-3

Peak (cm^{-1})	Group	Type of vibration
3003-3008	νCH	C=C-H , CH - stretching
2955±1	ν_{as}CH$_3$	Methyl Antisymmetric Stretching
2924±2	ν_{as}CH$_2$	Methylene Antisymmetric Stretching
2854±1	ν_sCH$_2$	Methylene Symmetric Stretching
1746±1	ν_sC=O	Aliphatic Carbonyl Stretching
1465	δCH$_2$	Methylene scissoring
1459	δ_{as}CH$_3$	Methyl Antisymmetric bending
1418±1	δCH	C=C-H , CH - in-plane bending
1377±1	δ_SCH$_3$	Methyl symmetric bending
1100-1240	Triplet with a maxima at 1162±1cm^{-1} flanked by a doublet at right side and a singlet at left side.	Triglyceride of long chain fatty acids
967±1	δCH	C=C-H CH bending out of plane
723±1	ρCH$_2$	Methylene rocking

Infrared spectra are shown in figures b.1 – b.9.
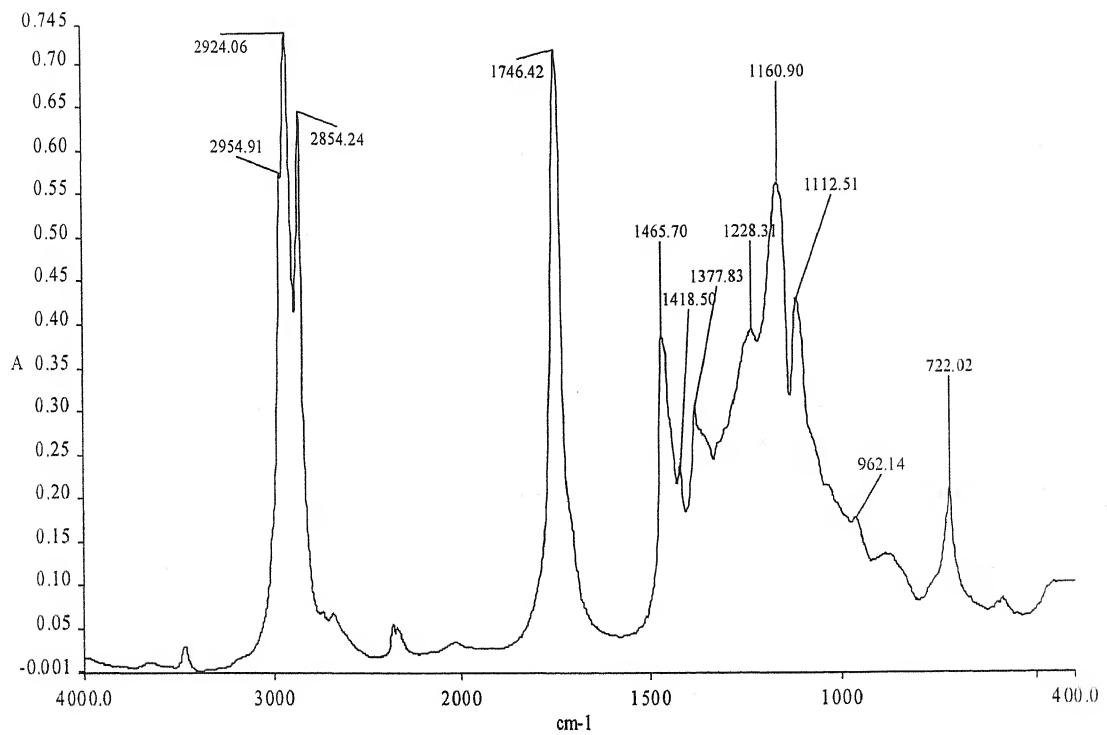
Fig.b.1-Coconut Oil
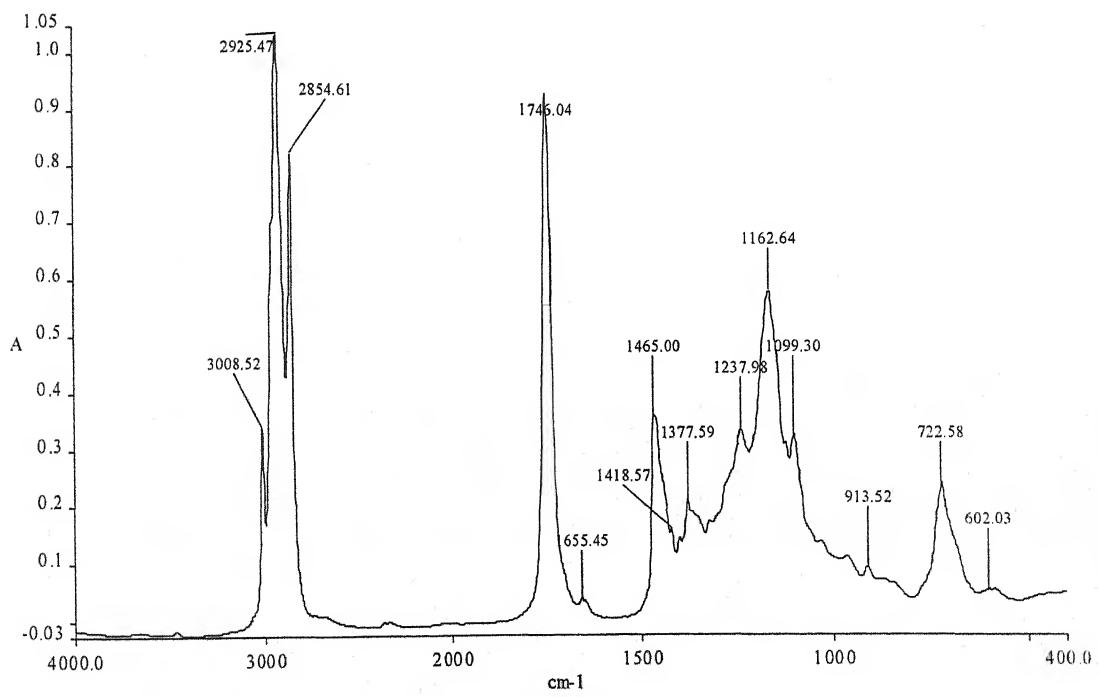
Fig.b.2-Sunflower Oil
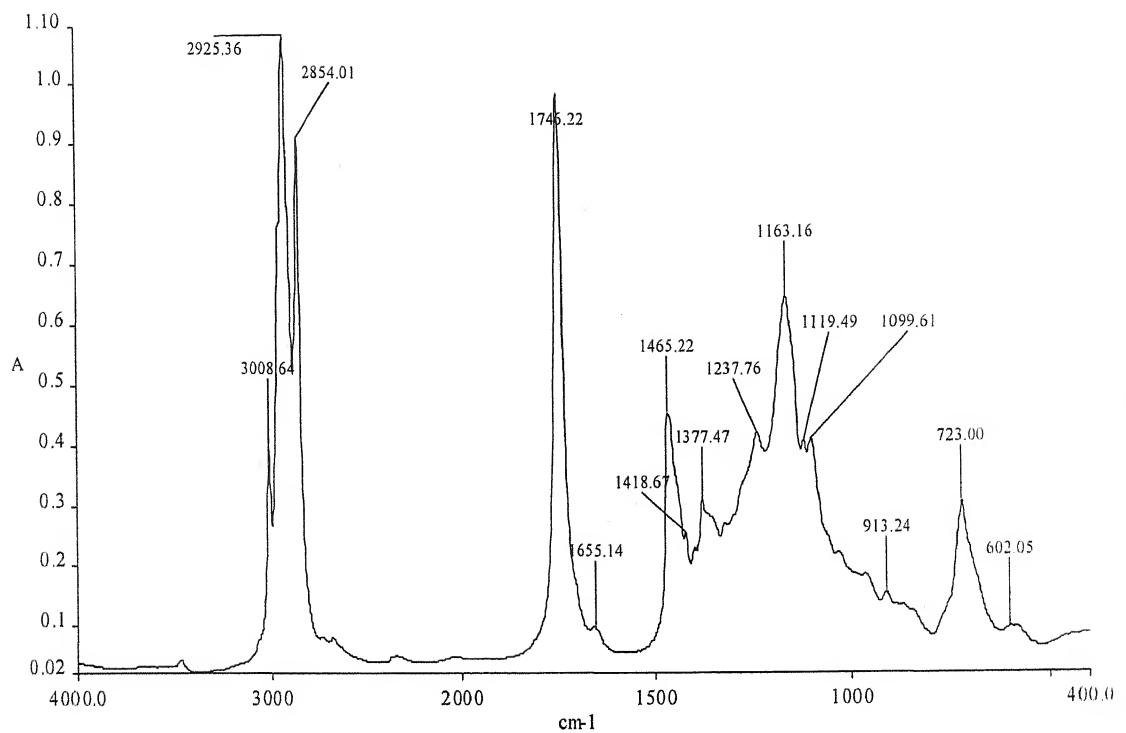
Fig.b.3-Cottonseed Oil
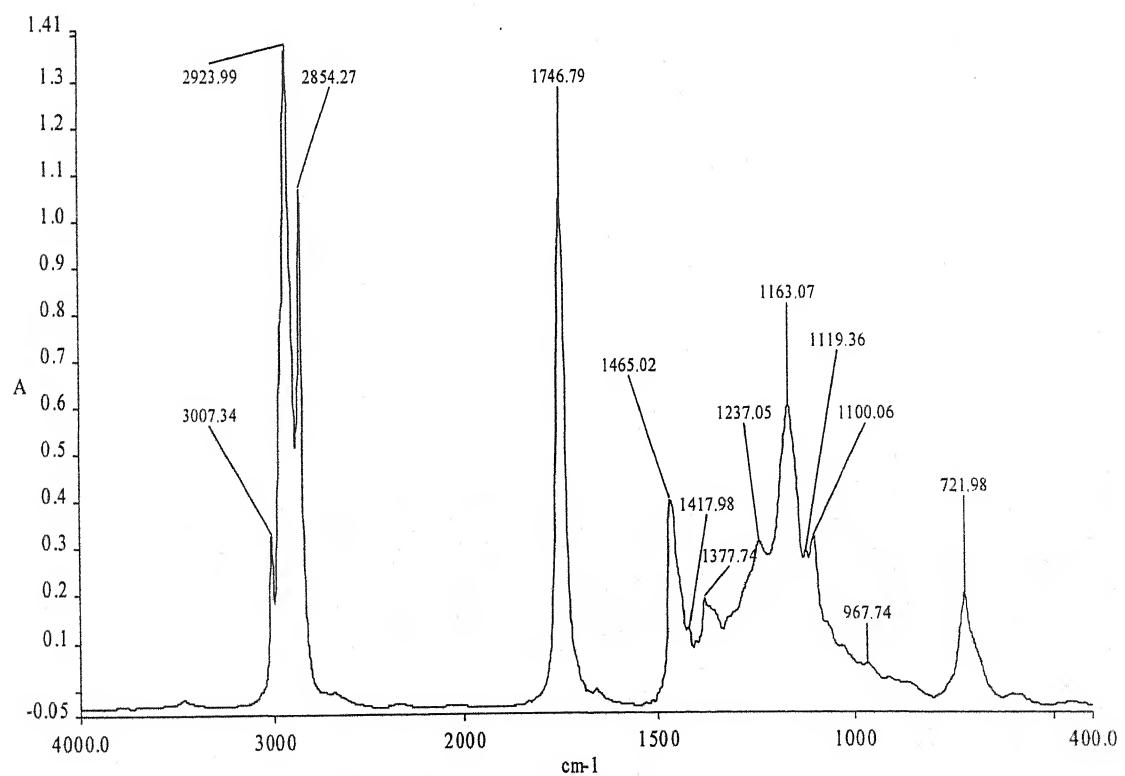
Fig.b.4-Mustard Oil
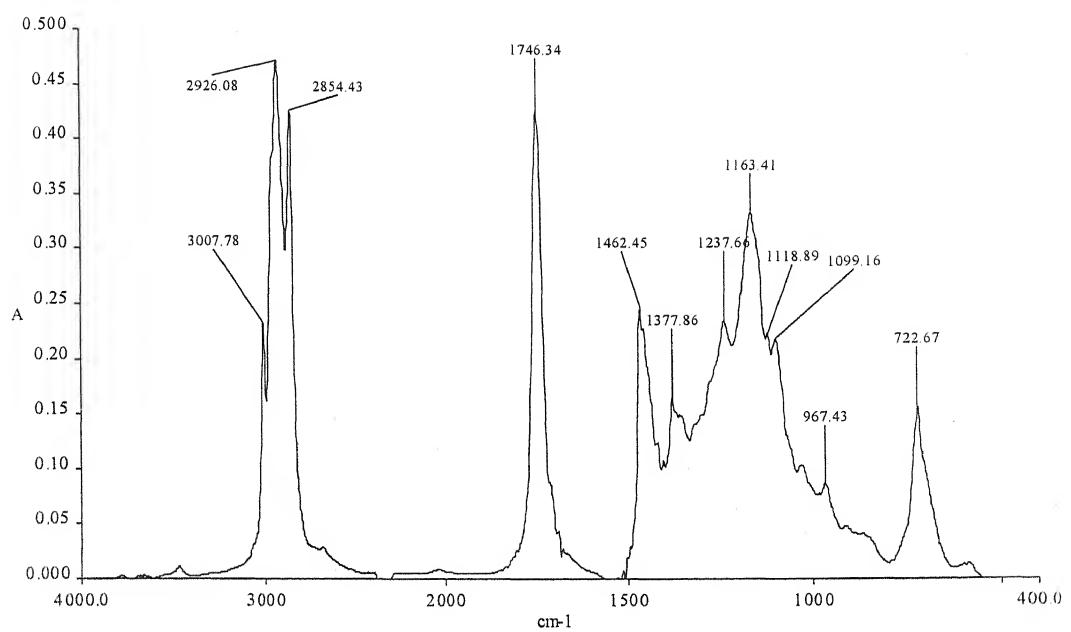
Fig.b.5-Rapeseed Oil
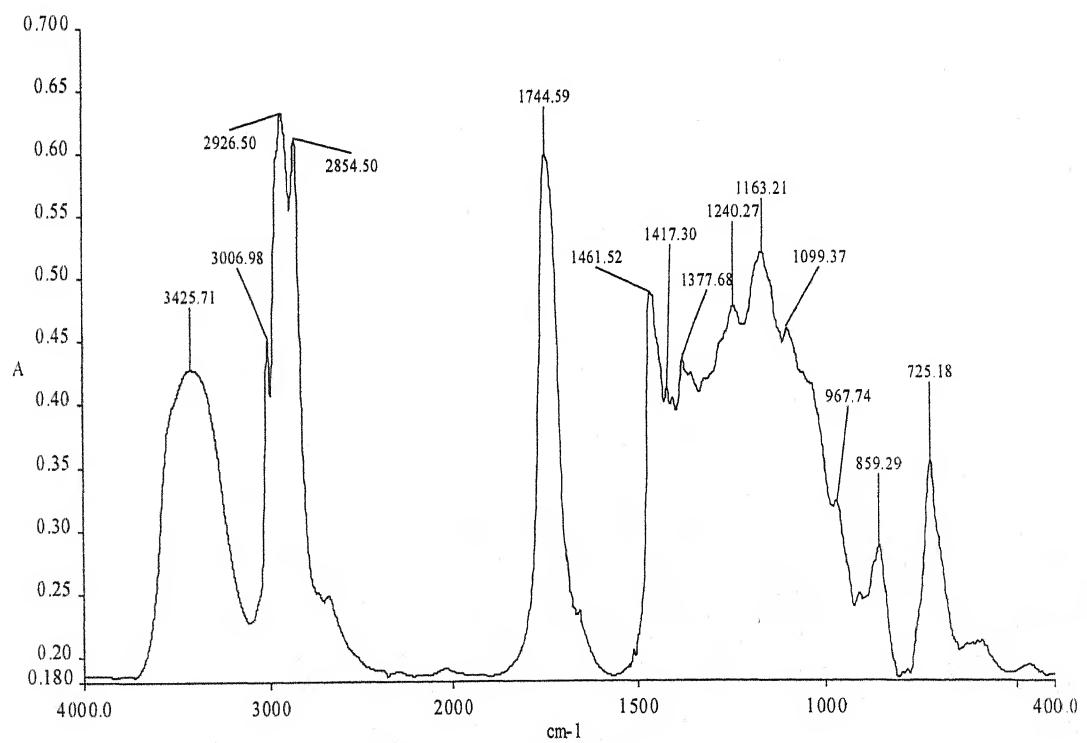
Fig.b.6-Castor Oil
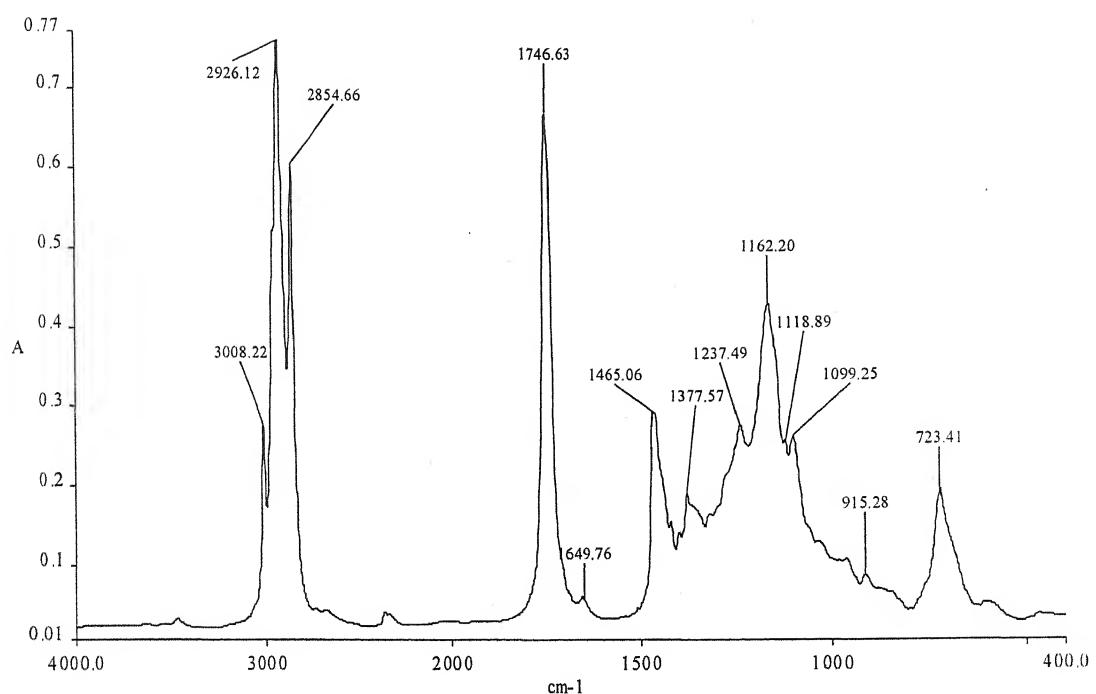
Fig.b.7- Kardi & Corn Blend Oil
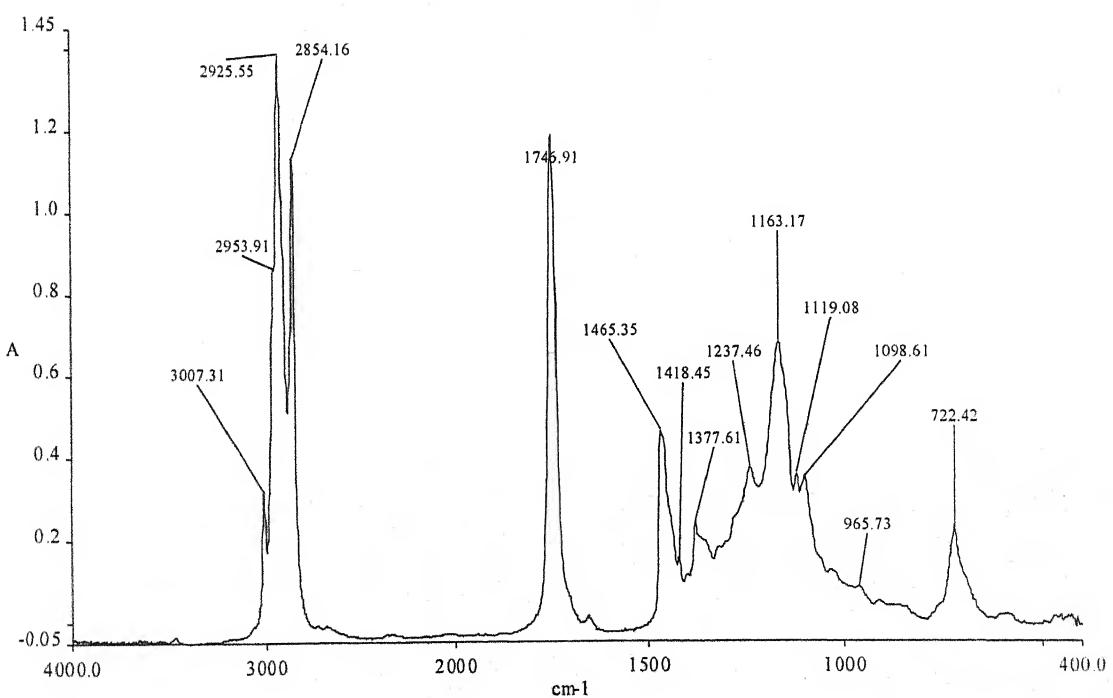
Fig.b.8-Groundnut Oil
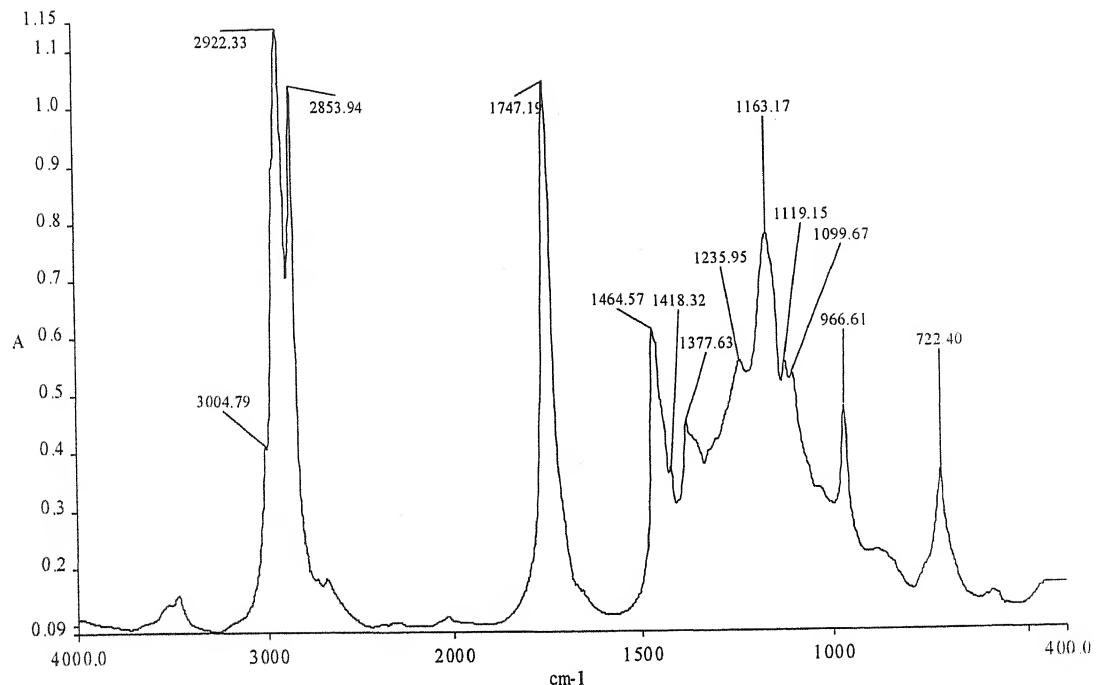
Fig.b.9-Vegetable Fat

(c) Spectra of substances of Animal Origin

Spectra of Lard and Milk Fat were found similar to that of the spectra of vegetable oils with respect to strong absorption bands. A spectrum of milk concentrate contains broad bands forming humps. Spectrum of honeybee wax contains carbonyl-stretching band at 1736 cm^{-1}, which is 10 cm^{-1} away from the absorption band of the same group found in other oils and fats. Absorption band due to triglyceride in honeybee wax contains only one peak at 1175cm^{-1}, which is also a weak band. Further split bands with doublet are found at 1473 cm^{-1} & 1464 cm^{-1} and 730 cm^{-1} & 720cm^{-1}. Spectra of Lard, Honeybee wax, Milk fat and Milk concentrate are as given in figures c.1 – c.4.
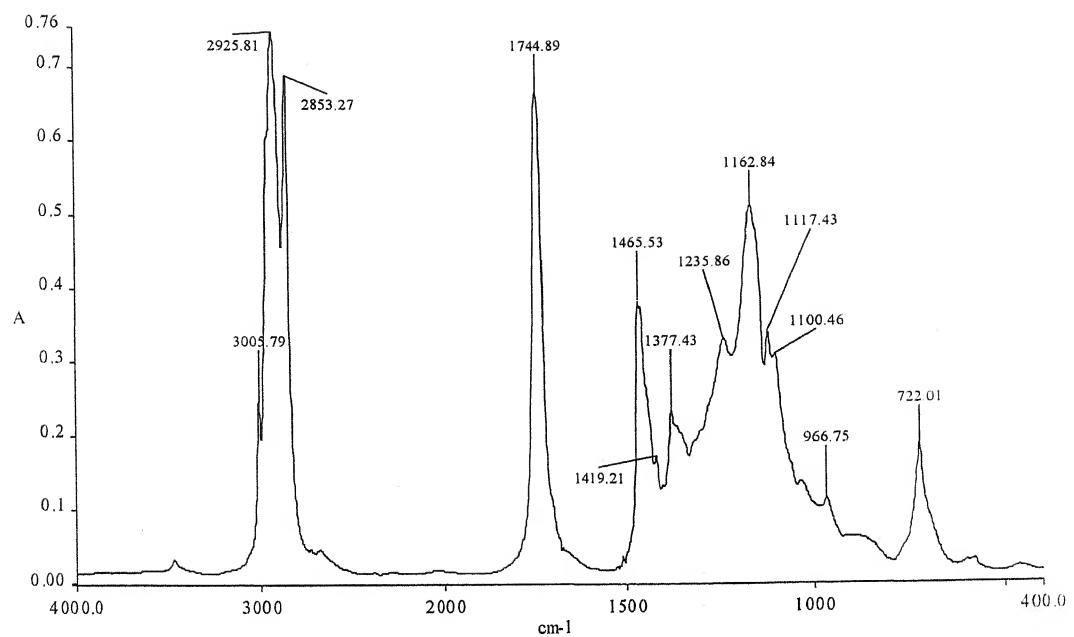
Fig.c.1-Lard Oil
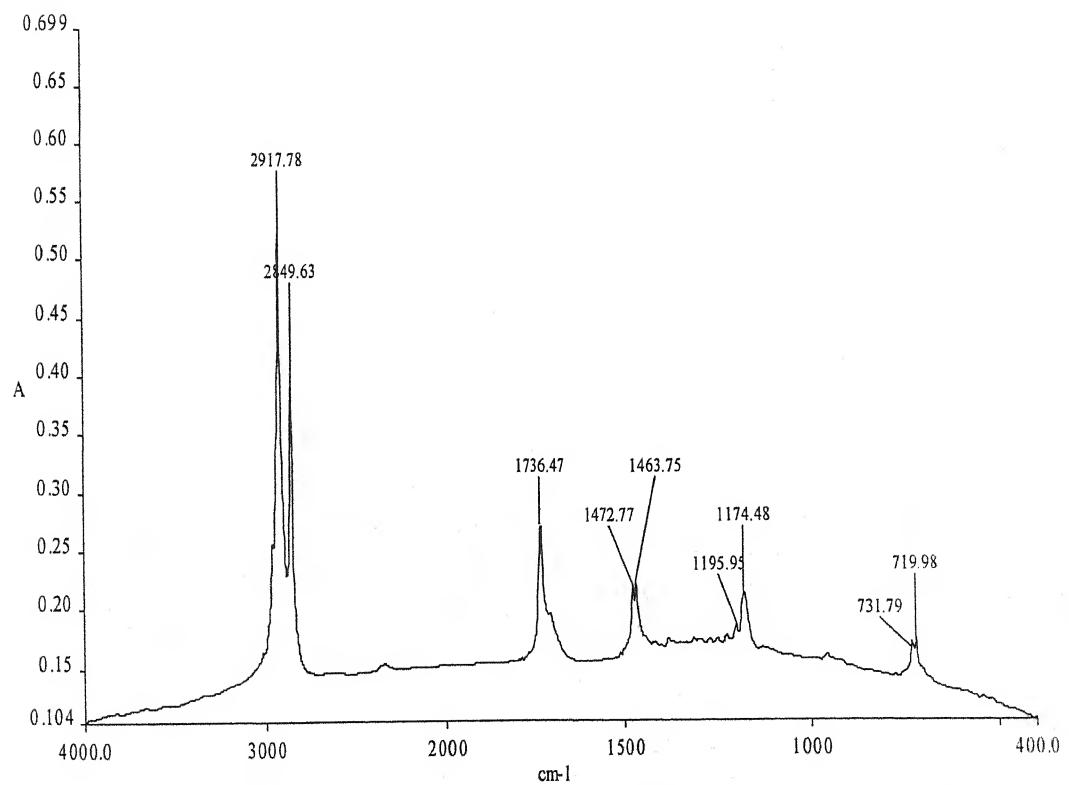
Fig.c.2-Honeybee Wax
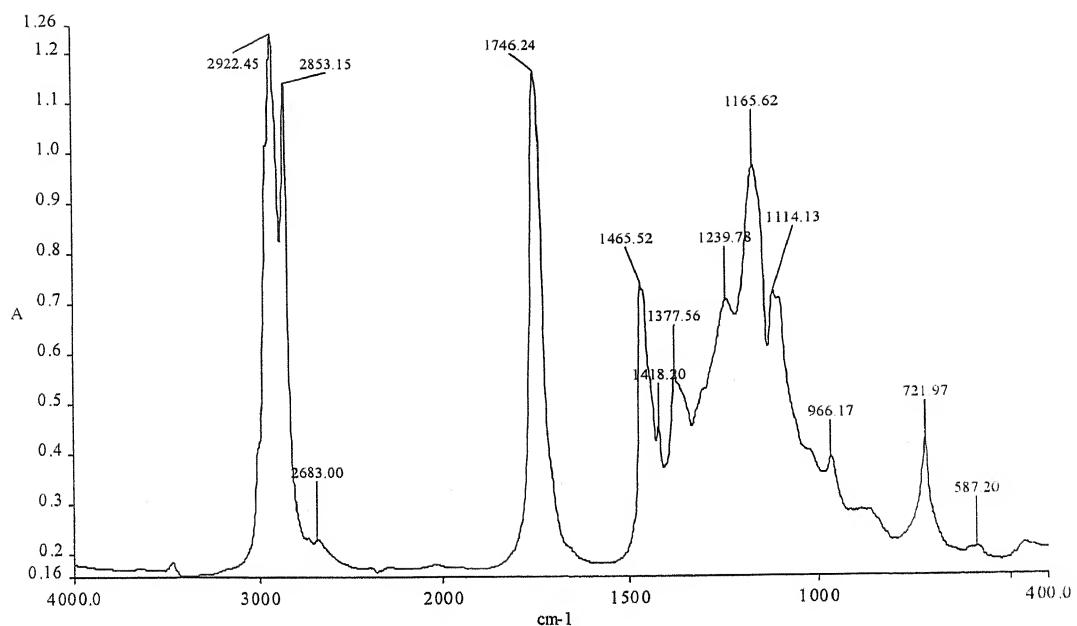
Fig.c.3-Milkfat
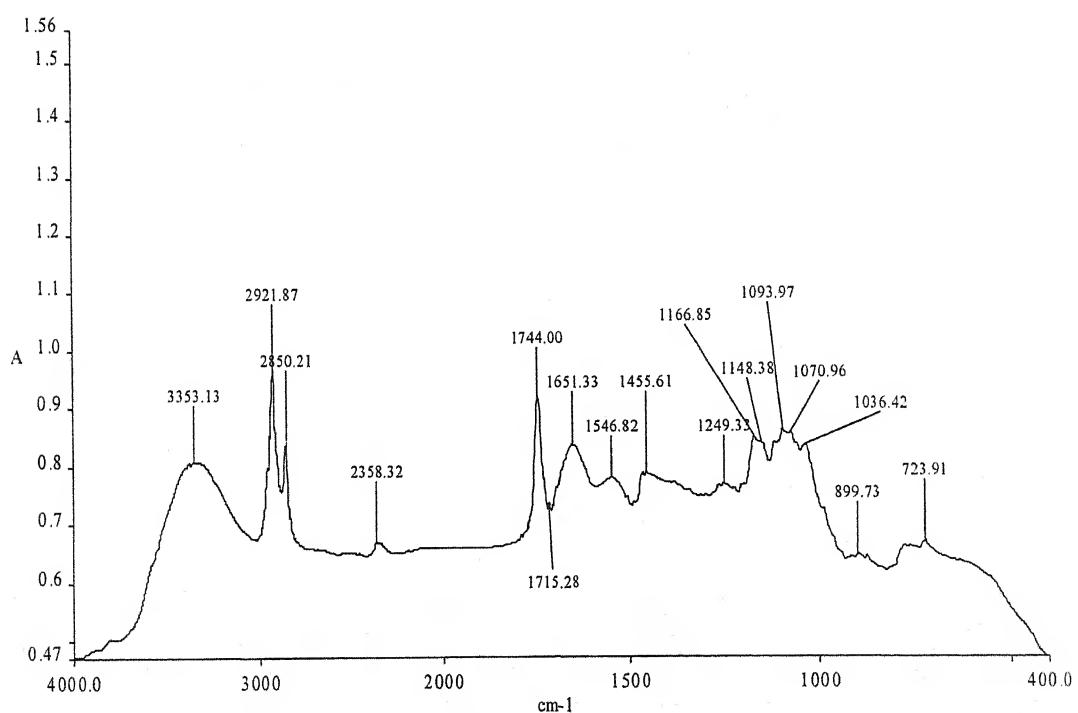
Fig.c.4-Khoya (Milk Concentrates)

(d) **Spectra of Sugars**

Spectra of Sugar, Shakkar (Brown sugar) and Gur (brown sugar lump form) also contain absorption peaks with broad humps as is evident from their spectra in figures d.1 – d.3.
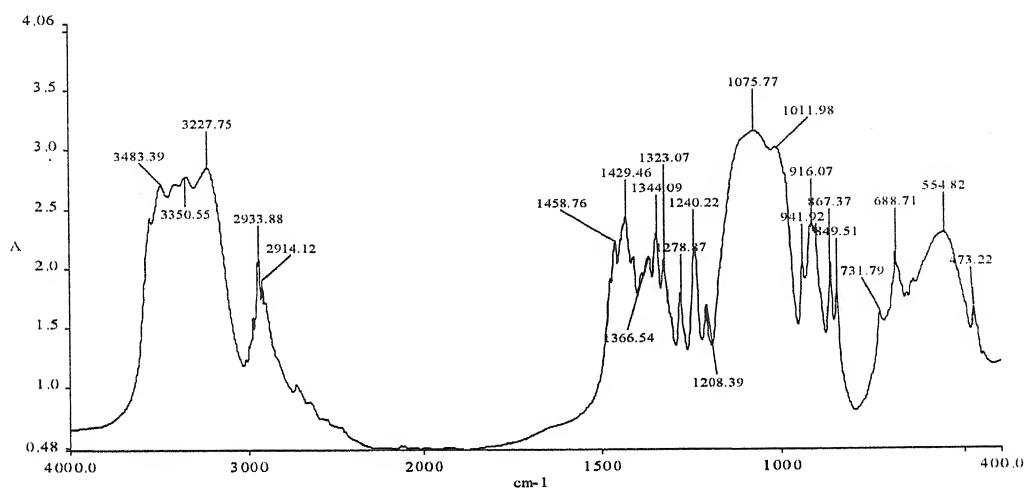
Fig.d.1-Sugar
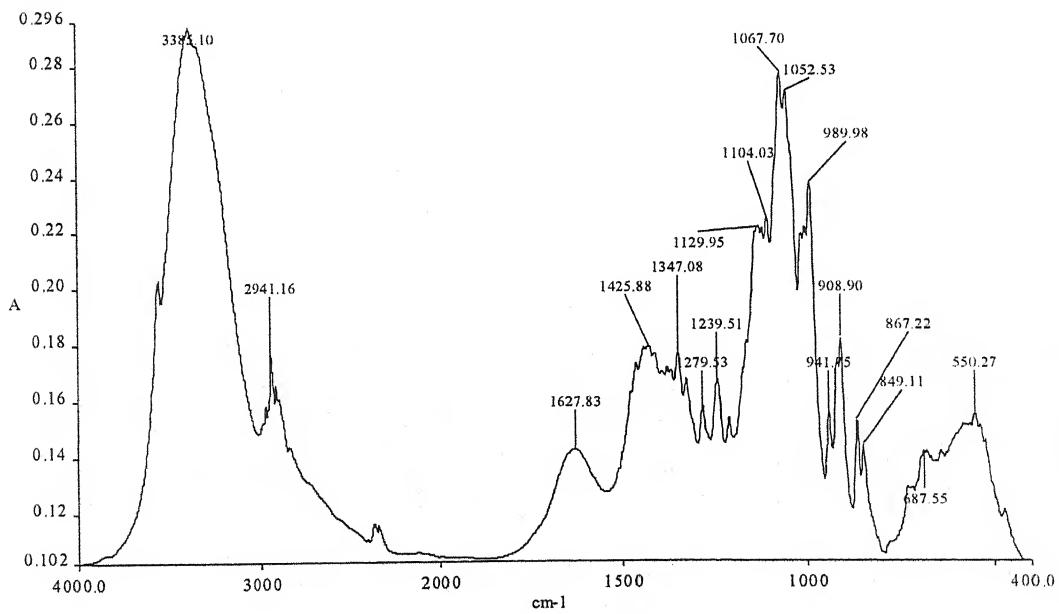
Fig.d.2-Brown Sugar
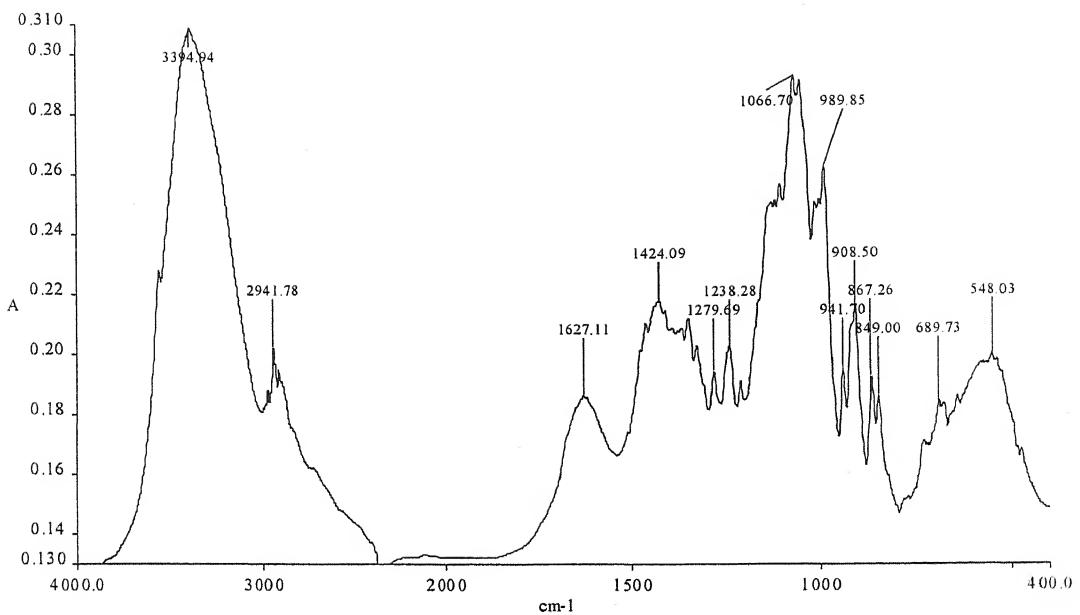
Fig.d.3-Lumps of Brown Sugar

(e) Spectra of Starches

Wheat flour, Maida and Gram flour show broad absorption bands in their Infrared spectra as can be seen in figures e.1 – e.3.
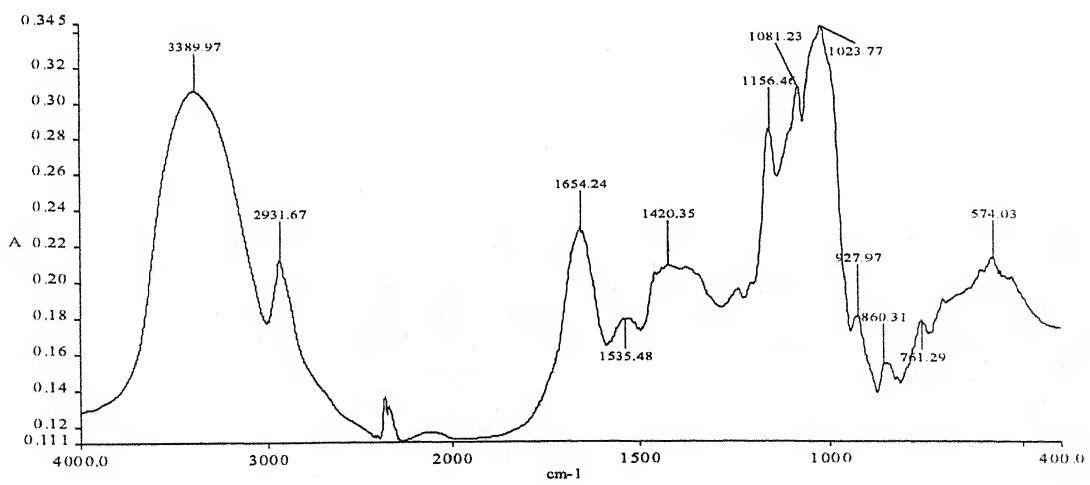
Fig.e.1-Wheat Flour
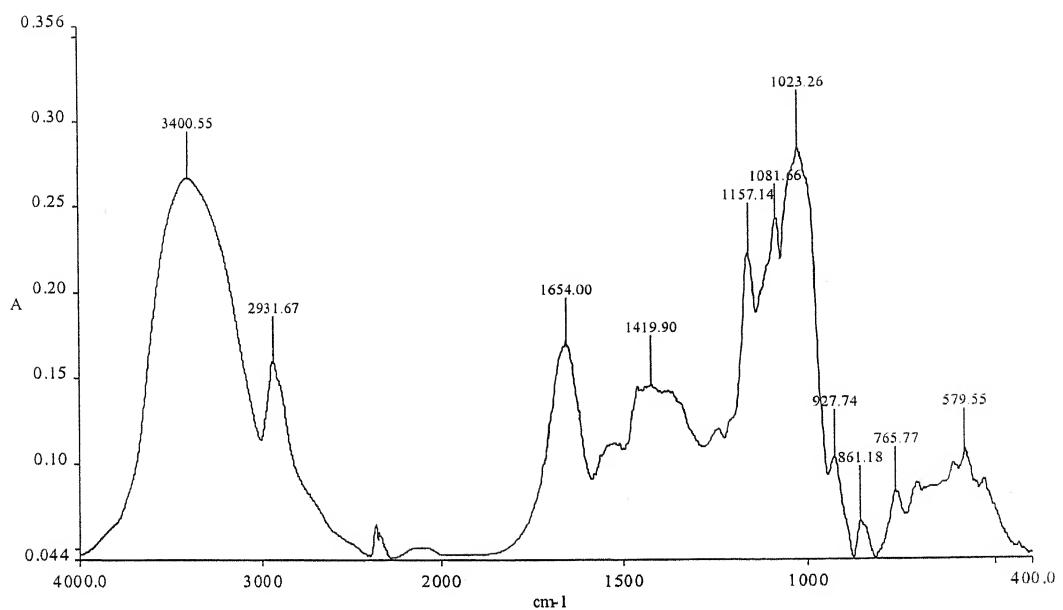
Fig.e.2 Maida (Fine Wheat Flour)
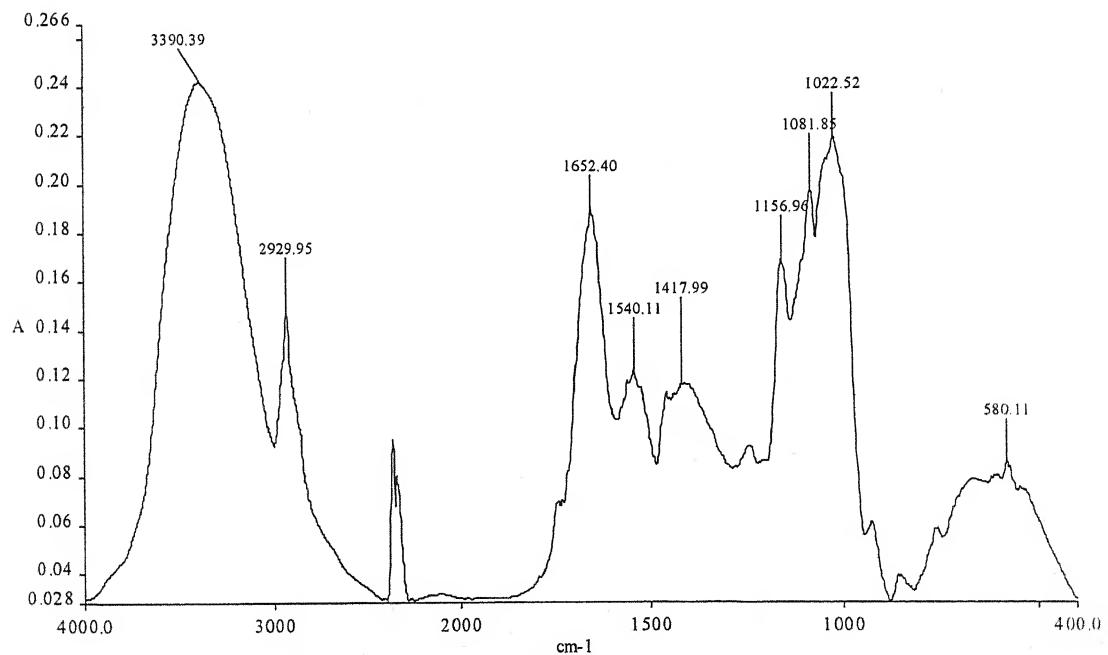
Fig.e.3- Gram Flour

(f) <u>**Spectra of Explosive Substances**</u>

Absorption peaks (cm^{-1}) of TNT, CE, PETN and RDX are given in Table-4, whereas their spectra are given in figures f.1- f.4. Infrared spectra of the above-referred explosive substances undertaken are also available (1, 85, 86, 87, 88, 89 and 90).
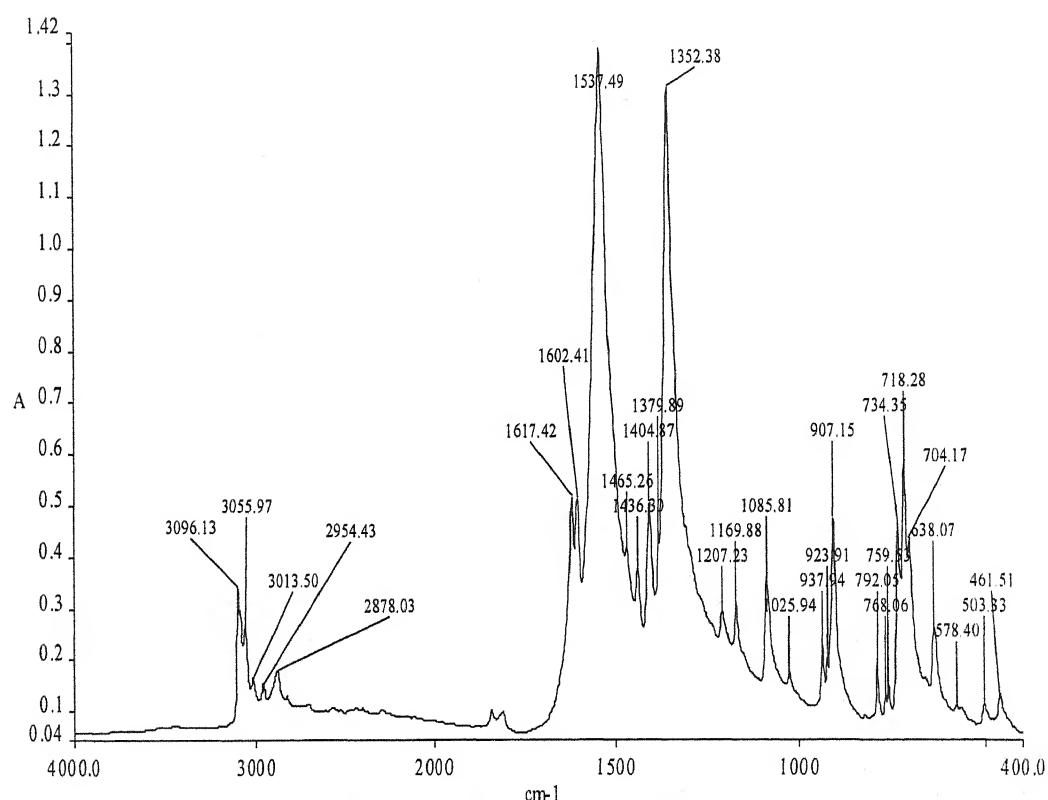
Fig.f.1-Trinitrotoluene (TNT)
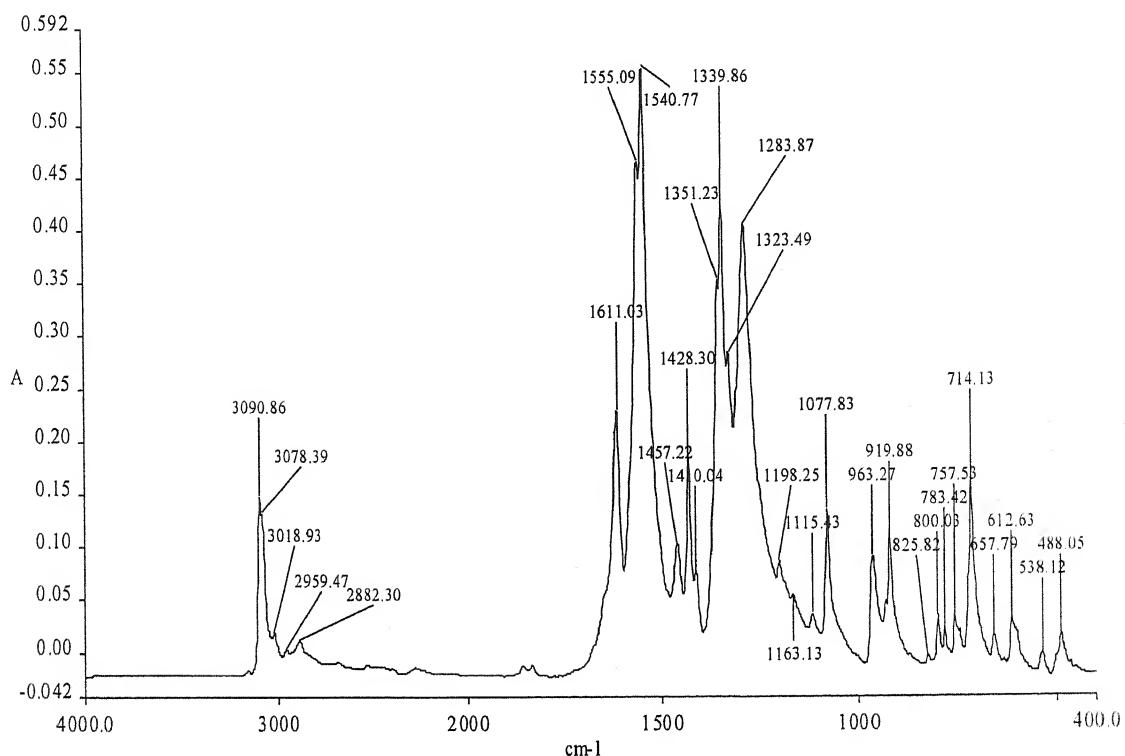
Fig.f.2-Tetryl (CE)
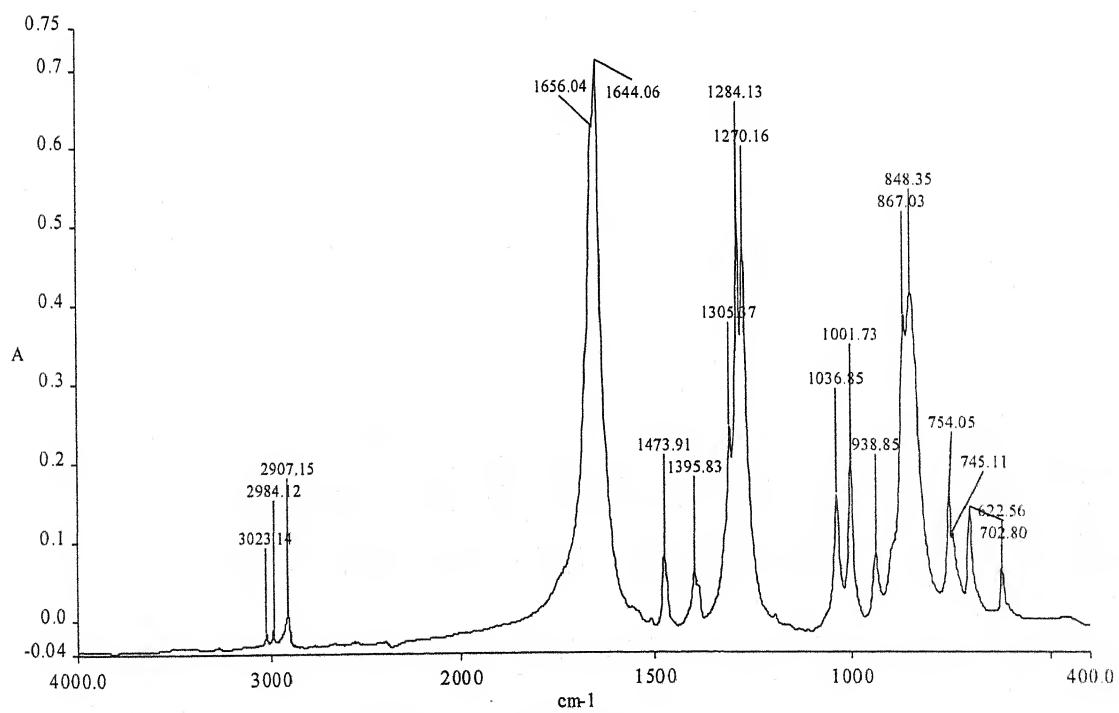


Fig.f.3-Pentaerythritol Tetranitrate (PETN)
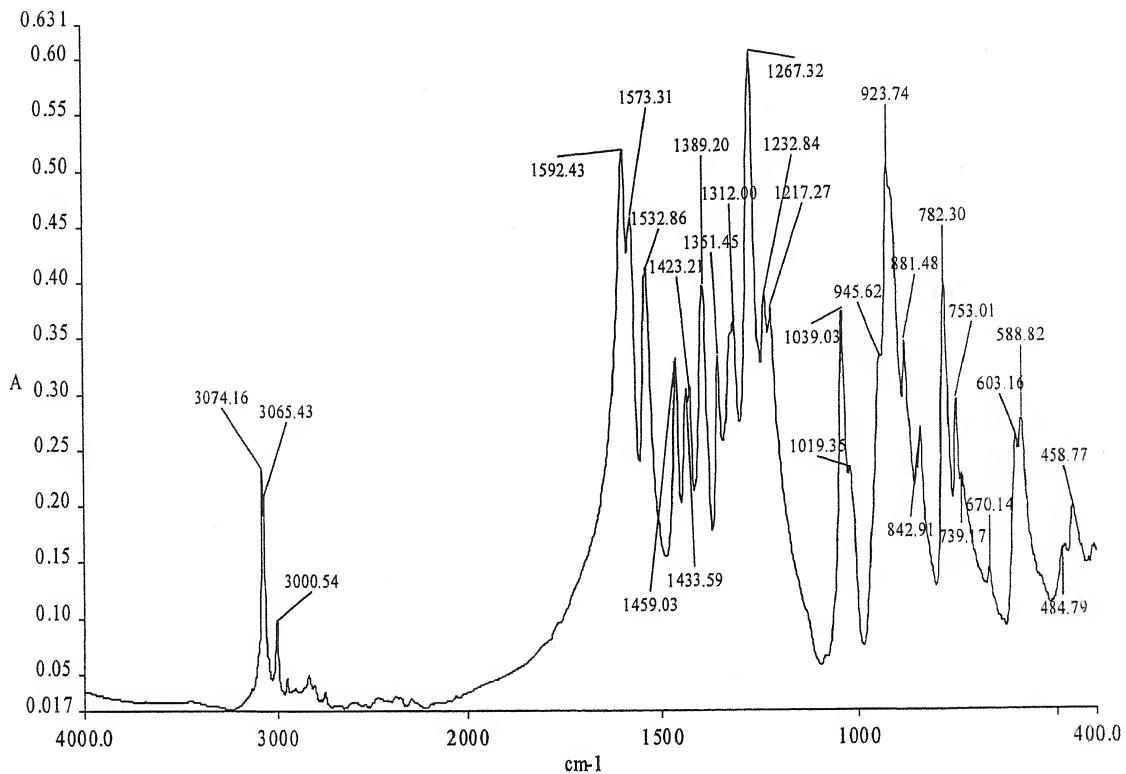
Fig.f.4-Cyclotrimethylentrinitramine (RDX)

TABLE-4

(All peak values rounded off to near digit)

Name of explosive Substances	Absorption bands (cm⁻¹)
TNT	3096, 3056, 1618, 1603, 1537, 1465, 1436, 1405, 1380, 1352, 1207, 1170, 1086, 1026, 938, 924, 907, 825, 792, 768, 760, 735, 718, 704, 662, 638, 578, 565, 503, 461

CE	3091, 3078, 3019, 1611, 1555, 1541, 1457, 1428, 1410, 1351, 1340, 1323, 1284, 1198, 1164, 1116, 1078, 963, 920, 826, 800, 784, 758, 714, 658, 613, 538, 488
PETN	3023, 2984, 2907, 1656, 1644, 1474, 1396, 1306, 1284, 1270, 1037, 1002, 939, 867, 848, 754, 745, 703, 623
RDX	3074, 3065, 3001, 1592, 1573, 1533, 1459, 1434, 1423, 1389, 1351, 1312, 1267, 1233, 1217, 1039, 1019, 945, 924, 881, 843, 782, 753, 737, 670, 603, 589, 479, 459

g) Mixtures of explosive substances with oils, fat, sugars and starches

MIXTURES OF TNT WITH DIFFERENT SUBSTANCES:

Infrared spectrum of gear oil (fig.a.4) depicts prominent peaks at 2952.cm^{-1} ($\nu_{as}CH_3$), 2924cm^{-1} ($\nu_{as}CH_2$), 2852 cm^{-1} (ν_sCH_2), 1461cm^{-1} ($\delta_{as}CH_3$), 1377 cm^{-1} (δ_s Methyl symmetric bending) and 722 cm^{-1} (ρCH_2). Only three peaks representing gear oil at 2952 cm^{-1} ($\nu_{as}CH_3$), 2924 cm^{-1} ($\nu_{as}CH_2$) and 2852 cm^{-1} (ν_sCH_2) can be seen in the spectrum of the mixture of TNT with gear oil (fig.g.4). Strong absorption peaks of gear oil at 1461

cm^{-1}, 1377 cm^{-1} and 722 cm^{-1} along with minor peaks at 1305 cm^{-1} and 1164 cm^{-1} have been found to be masked by the neighbouring strong absorption bands of TNT. All strong absorption bands representing TNT (fig.f.1) can be seen in the spectrum of mixture of TNT with gear oil as given in Table-5. Only very minor peaks at 3013 cm^{-1}, 2878 cm^{-1}, 768 cm^{-1} and 578 cm^{-1} seen in the spectrum of pure TNT (fig.f.1) could not be seen in the spectrum of mixture of TNT and Gear oil (fig.g.4). Same is also true with the spectra of samples of TNT with other petroleum products recorded as g.1 to g.11.

The characteristic peaks of groundnut oil (fig.b.8) indicating its category comprising triglycerides of long chain fatty acids are at 3007 cm^{-1} (Vinylic-CH stretching ν_s-C=C-H), 2926 cm-1 ($\nu_{as}CH_2$), 2854 cm^{-1} (ν_sCH_2), 1747 cm^{-1} ($\nu_sC=O$), four peaks at 1237 cm^{-1}, 1163 cm^{-1}, 1119 cm^{-1} and 1099 cm^{-1} indicating triglycerides and 722 cm^{-1} (ρCH_2). Prominent peaks of groundnut oil at 2927 cm^{-1}, 2854 cm^{-1} and 1749 cm^{-1} can be seen in the spectrum of mixture of TNT and groundnut oil (fig.g.52). Remaining peaks of groundnut oil including the characteristic peaks representing triglyceride are not visible in the spectrum of mixture containing about 10% concentration of groundnut oil. However, the very prominent and characteristic peak representing the carbonyl group of groundnut oil is present in the spectrum of mixture at 1749 cm^{-1}. Peak at about 1465 cm^{-1} and 1379 cm^{-1} are common both in TNT and groundnut oil, which are also

appearing in the spectrum of mixture of both substances. All the peaks of TNT (fig.f.1) are present in the spectrum of mixture of TNT and groundnut oil (fig.g.52) except the minor peaks at 825 cm^{-1} and 662 cm^{-1}. Hence, presence of characteristic bands, in the spectrum of mixture of TNT and groundnut oil gives fair indication of vegetable oil and absolute identification of TNT as given in Table-6.

In case of spectra of mixtures of TNT with other substances recorded as g.45 to g.53, g.81, g.85, g.89 and g.93 with oils of vegetable and animal origin, similar pattern is observed as in the case of TNT and groundnut oil. Even characteristic peak representing C=O group in honey bee wax at 1737 cm^{-1} can be seen in the spectrum of mixture of TNT and honey bee wax (g.85). TNT couldn't form a pasty material with milk concentrate in the ratio of 9:1. It has been observed that TNT forms a mouldable mixture with milk concentrate on mixing both the substances approximately in 3:1 ratio. In the spectrum of combination of such a mixture (fig.g.93), TNT can be easily identified. In addition, one gets a fair indication of the presence of milk concentrate in the mixture also. However, the spectrum (fig.g.93) is recorded by mixing TNT with milk concentrate in equal ratio, which indicates that TNT even in the presence of equal quantity of milk concentrate can be identified in the mixture.

In the spectrum of honeybee wax with TNT (g.85), the triplet absorption band representing triglycerides of long chain fatty acids is also

missing. From spectra of mixtures of TNT with sugars and starches, it is possible to identify explosive substance TNT in addition to indication of sugar or starch. It is another matter that the substances contained in category of sugars and starches do not form mouldable mixtures with TNT.
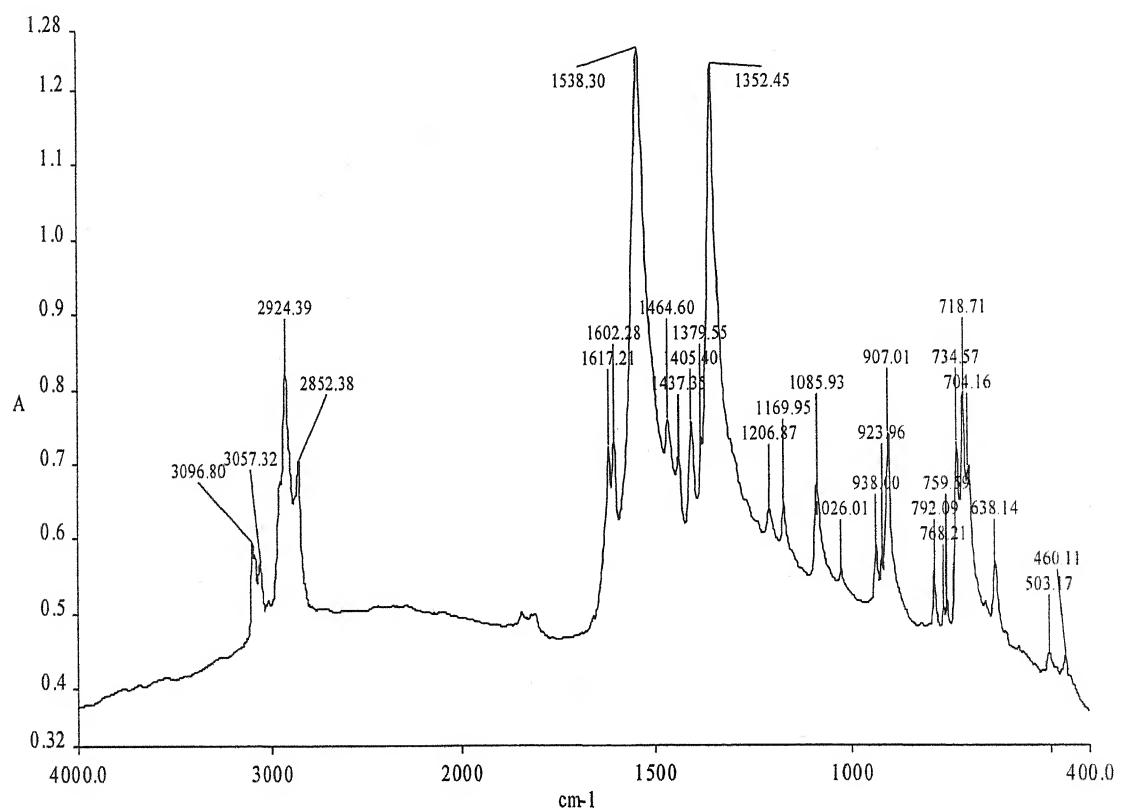

Fig.g.4-TNT+ Gear Oil
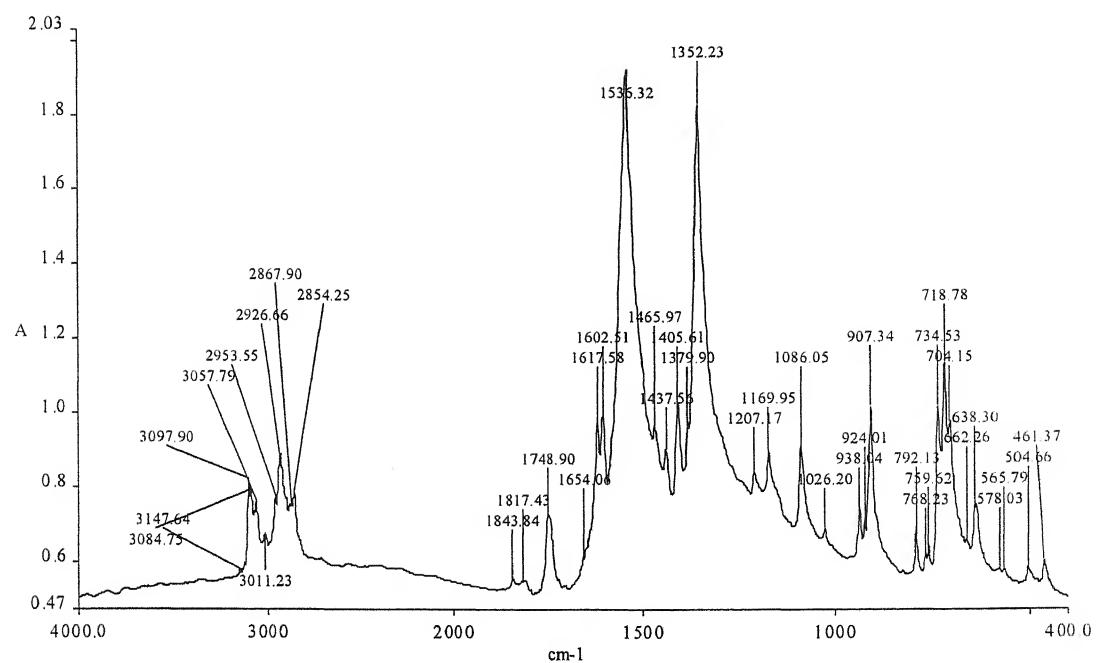
Fig.g.52-TNT + Groundnut Oil
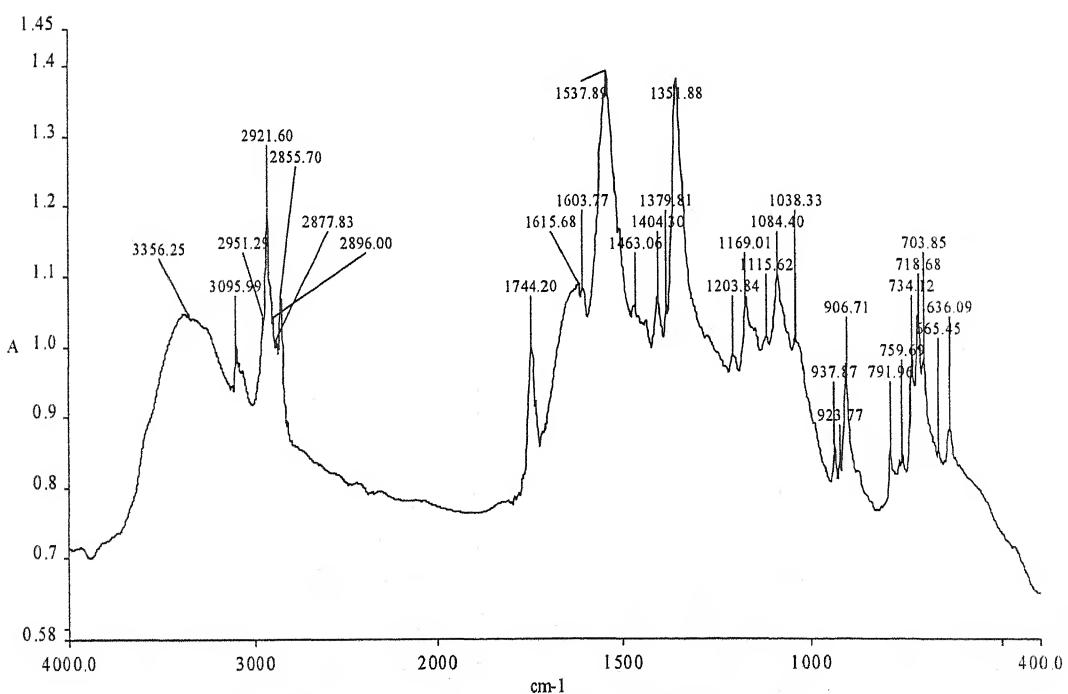
Fig.g.93-TNT + Milk concentrates
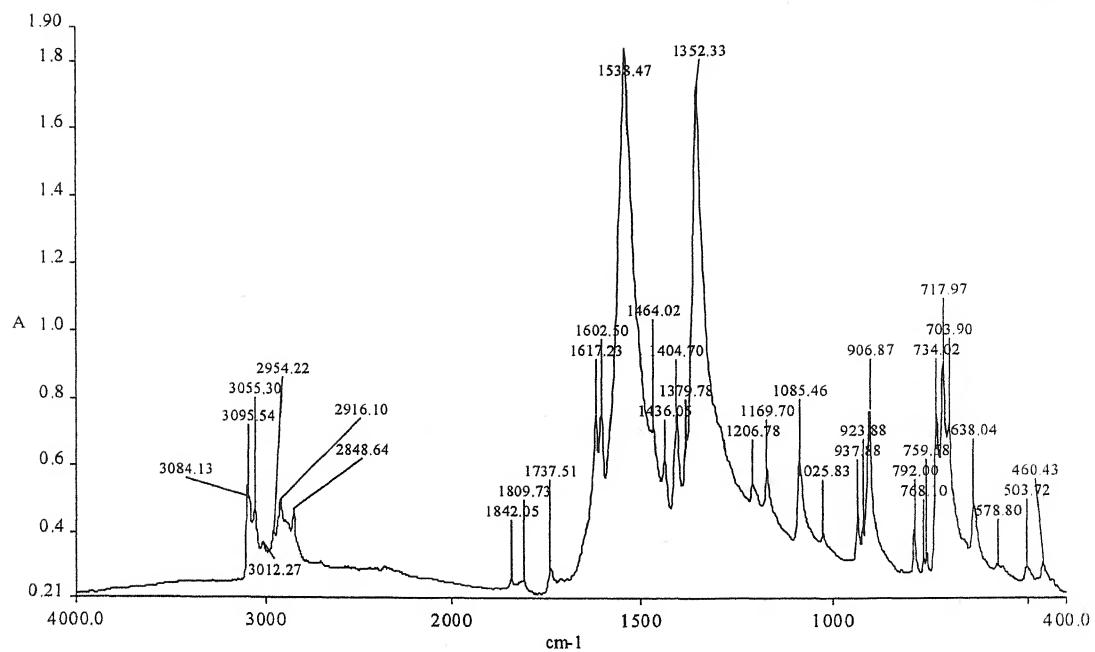
Fig.g.85-TNT + Honeybee Wax

TABLE-5

(All peak values rounded off to near digit)

TNT + Gear oil (cm⁻¹)	TNT (cm⁻¹)	Gear oil (cm⁻¹)
3097	3096	
3057	3056	
	3013	
	2955	
2925		2924
	2878	
2852		2852
1617	1618	
1602	1603	

1538	1537	
1464	1465	
		1461
1437	1436	
1406	1405	
1380	1380	
		1377
1353	1352	
		1305
1207	1207	
1170	1170	
		1164
1086	1086	
1026	1026	
938	938	
924	924	
907	907	
792	792	
	768	
760	760	
735	735	
		722
719	718	
704	704	
638	638	
503	503	
461	461	

TABLE-6

(All peak values rounded off to near digit)

TNT + Groundnut oil (cm^{-1})	TNT (cm^{-1})	Groundnut oil (cm^{-1})
3098	3096	
3058	3056	
3011	3013	
		3007
2954	2955	2954
2927		2926
	2878	
2868		
2854		2854
1749		1747
1618	1618	
1603	1603	
1536	1537	
1466	1465	1465
1438	1436	
		1418
1406	1405	
1380	1380	
		1378
1352	1352	
1207	1207	
		1237

1170	1170	
		1163
		1119
		1099
1086	1086	
1026	1026	
		966
938	938	
924	924	
907	907	
792	792	
769	768	
760	760	
735	735	
		722
719	718	
704	704	
638	638	
578	578	
565		
504	503	
461	461	

MIXTURES OF TETRYL (CE) WITH DIFFERENT SUBSTANCES:

Tetryl and TNT are very close in structure except that in tetryl one of the substituent in aromatic ring is methylnitramine, whereas in TNT it is methyl group. This difference in substitution has produced a shift in many absorption bands, which represent similar chemical entities in both TNT and Tetryl. However, absorption bands at 1284 cm^{-1} (N-N ν_s), 1323 cm^{-1} (Aromatic 3^0 amine), a shoulder in between absorption bands 1340 cm^{-1} & 1284 cm^{-1} and 1457 cm^{-1} (CH_3-N deformation) are characteristic to tetryl only and are found invariably in spectra of mixtures of oils of petroleum and vegetable origin with tetryl.

Data of absorption bands detected in Infrared spectrum of a mixture of tetryl with heavy paraffin oil (fig.g.13) and with coconut oil (fig.g.54) is given in Table Nos.7 and 8. It shows absorption bands derived from Tetryl and oil present in the spectra of their mixture. Tetryl is easy to identify from the spectra of its mixture with different substances comprising tetryl and oils of petroleum and animal origin, wax and fat. The spectra of mixtures give fair indication of additives like oils of petroleum and animal origin, wax, and fat. Spectra of tetryl with petroleum substances have been recorded as g.12 to g.22 and with other vegetable oils & fats etc. as g.54 to g.62, g.82, g.86, g.90 and g.94.
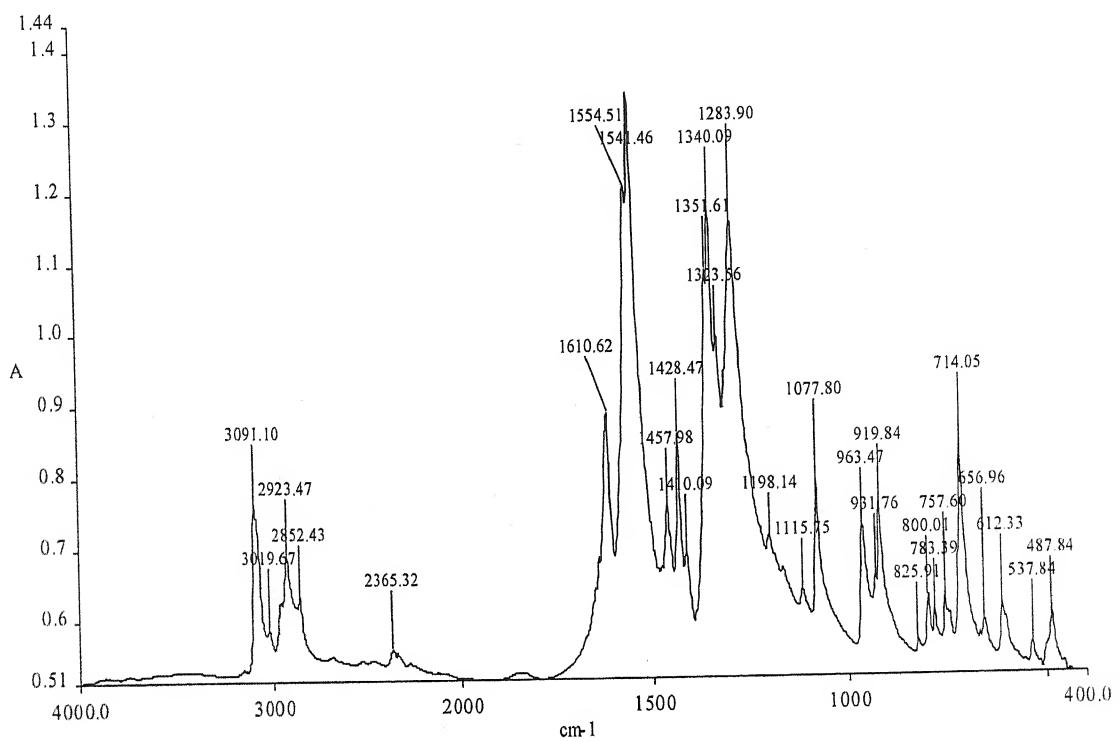
Fig.g.13-CE + Paraffin Oil
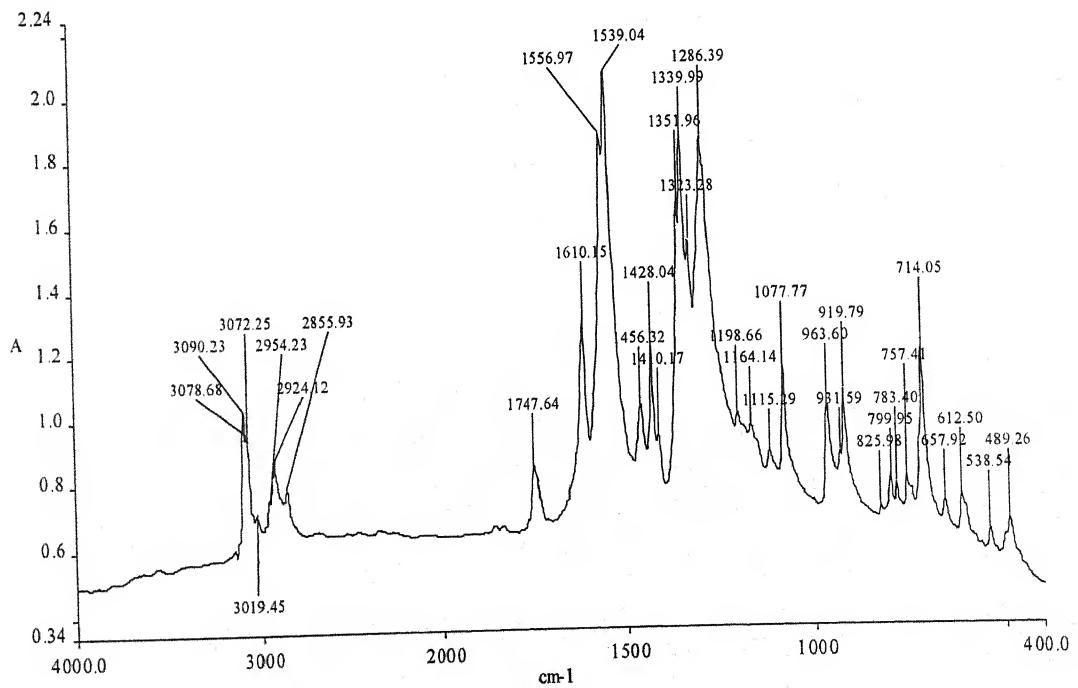

Fig.g.54-CE + Coconut Oil
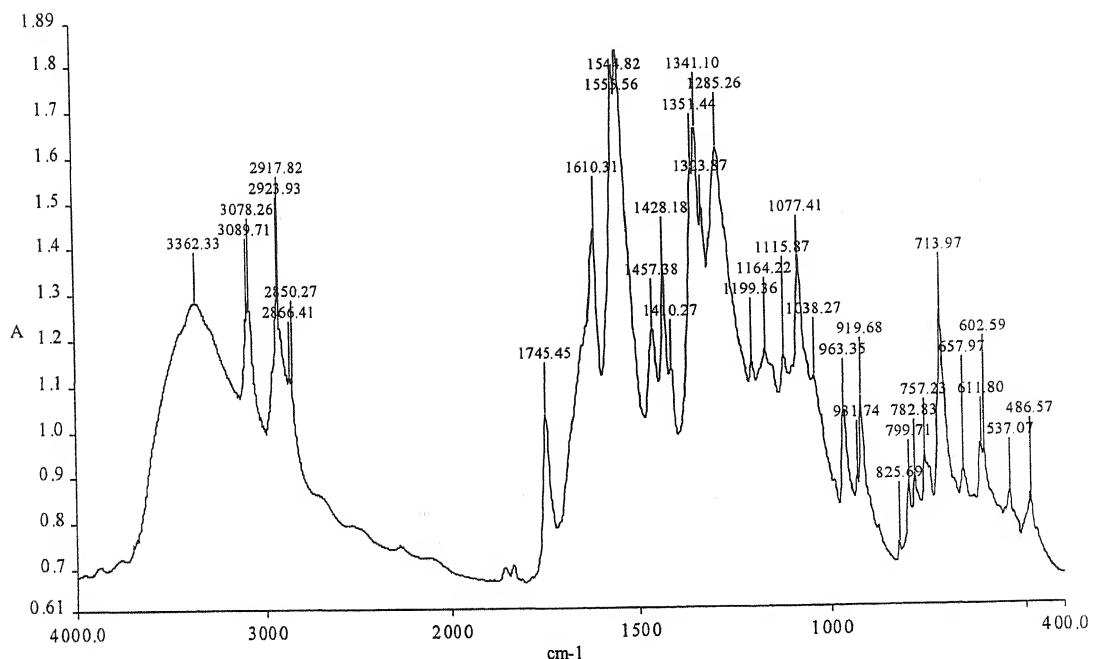
Fig.g.94-CE + Milk concentrates

TABLE-7

(All peak values rounded off to near digit)

Tetryl + Paraffin (cm⁻¹)	Tetryl (cm⁻¹)	Paraffin oil (cm⁻¹)
3091	3091	
	3078	
3020	3019	
	2959	
		2930
2924		
		2915
	2882	
2852		2854

1611	1611	
1555	1555	
1541	1541	
1458	1457	1460
1428	1428	
1410	1410	
		1377
1352	1351	
1340	1340	
1324	1323	
		1305
1284	1284	
1198	1198	
		1155
1116	1116	
1078	1078	
963	963	
932		
920	920	
826	826	
800	800	
783	784	
758	758	
		722
714	714	
657	658	
612	613	

538	538	
488	488	

TABLE-8

(All peak values rounded off to near digit)

Tetryl + Coconut oil (cm^{-1})	Tetryl (cm^{-1})	Coconut oil (cm^{-1})
3090	3091	
3078	3078	
3019	3019	
2955	2959	2955
2924		2924
	2882	
2856		2854
1748		1747
1610	1611	
1557	1555	
1539	1541	
		1466
1457	1457	
1428	1428	
		1418
1410	1410	
1352	1351	
		1378
1340	1340	
1323	1323	

1286	1284	
1199	1198	
		1228
1164	1163	1161
1115	1116	1112
1078	1078	
964	963	962
920	920	
826	826	
800	800	
783	784	
758	758	
		722
714	714	
658	658	
613	613	
539	538	
489	488	

MIXTURES OF PETN WITH DIFFERENT SUBSTANCES:

Spectrum of mixture of PETN + HSD (fig.g.23) is compared with the individual spectrum of PETN (fig.f.3) and HSD (fig.a.1). From the data given in Table-9, it can be seen that one peak of HSD at 2955 cm^{-1} due to methyl anti-symmetric stretching and two absorption peaks at 2924 cm^{-1} and

2854 cm^{-1} due to methylene antisymmetric and symmetric stretching could be easily identified in the spectrum of mixture of PETN and HSD. On the other hand all peaks of PETN could be seen in the spectrum of mixture of PETN + HSD.

Peaks at 1664 cm^{-1} and 1193 cm^{-1} appearing in the spectrum of PETN + HSD are not present in the spectra of either PETN or HSD. Similarly, peaks marked with asterisks (*) in the column of table-9 of HSD could not be identified in the spectrum of PETN + HSD. It is due to the fact that quantity of diesel in the mixture has been reduced to approximately 10%, which ultimately resulted in the reduction of intensity of these peaks in the spectrum of mixture of PETN and HSD. Only two prominent characteristic peaks representing methylene antisymmetric (2922 cm^{-1}) and symmetric stretching (2854 cm^{-1}) present in the spectrum of PETN + HSD, indicated the presence of long chain hydrocarbons comprising repeated methylene units. Hence, from spectra recorded as g.23 to g.33 it has been observed that detection of PETN in the presence of any of the substances mentioned in the list with heading Petroleum origin is easily possible.

The absorption peaks in the spectrum of PETN +Mustard oil (fig.g.66) recorded in the ratio of 9:1 ratio for the detection of absorption peaks due to PETN (fig.f.3)and Mustard oil (fig.b.4) are as given Table-10.

First two absorption bands due to PETN at 3023 cm^{-1} and 2984 cm^{-1} are still present in the spectrum of mixture of PETN and mustard oil in spite

of the fact that very strong absorption bands due to Methylene antisymmetric stretching and symmetric stretching comprising long chain fatty acids at 2922 cm^{-1} & 2854 cm^{-1} are present in this region of electromagnetic radiation. These two strong absorption bands of mustard oil could mask the peak of PETN at 2907 cm^{-1}. Remaining all of the prominent peaks of PETN can be seen in the spectrum of mixture of PETN + Mustard oil. Vegetable oil can be clearly identified in the spectrum of PETN + Mustard oil from characteristic peaks at 2922 cm^{-1} ($\nu_{as}CH_2$), 2854 cm (ν_sCH_2), 1746 cm^{-1} (C=O stretch) and, 1161cm^{-1}. Absorption peaks of PETN in that range of spectrum have masked other absorption peaks representing mustard oil. Same is also true in case of the spectra of PETN mixtures recorded as g.63 to g.71, g.83, g.87, g.91 and g.95 formed by combination with other vegetable oils, vegetable fat and other products of animal origin including lard, milk fat, honey bee wax and milk concentrate. PETN can be easily detected in the spectra of their mixtures with oil / fat of vegetable or animal origin.

In a mixture of Milk concentrate with PETN (fig.g.95), the spectrum indicates a peak at 1745 cm^{-1} which is again reflecting the presence of C=O group. Further, an absorption peak at 1167 cm^{-1} flanked by small peaks at 1192 cm^{-1}, 1116 cm^{-1} and 1095 cm^{-1} indicated the presence of triglyceride. The spectra of mixture of PETN + Milk concentrate also indicated a strong broad hump near about 3370 cm^{-1} and absorption bands at 2922 cm^{-1} and

2852 cm^{-1} representing Methylene Antisymmetric and symmetric stretching respectively. These absorption bands are also present in the spectrum of milk concentrate (fig.c.4). The spectrum of mixture of PETN + Milk concentrate (fig.g.95) comprises numerous sharp absorption bands. From the other peaks in this spectrum, PETN can be easily identified. Many absorption peaks of PETN look prominent and distinguished above the broad absorption peaks of milk concentrate. Hence, it is possible to identify PETN in milk concentrate even when the quantity of PETN in the combination has been reduced down to 50%.

The series comprising sugars containing sugar, brown sugar and lump brown sugar and starch containing wheat flour, maida and gram flour individually lack binding capacity when mixed with PETN. Spectra of mixtures of PETN mixed with these substances were also studied. It has been observed that detection of PETN by the method of spectroscopy in these mixtures is possible. In spite of the fact that sugars and starches produce many absorption bands, which mask or obscure the peaks of explosive substances, still identification of explosive substance is possible. Hence it is possible to detect PETN when mixed with petroleum products, oils and fat of vegetable or animal origin, crude sugar products and starchy materials to create a disguise.
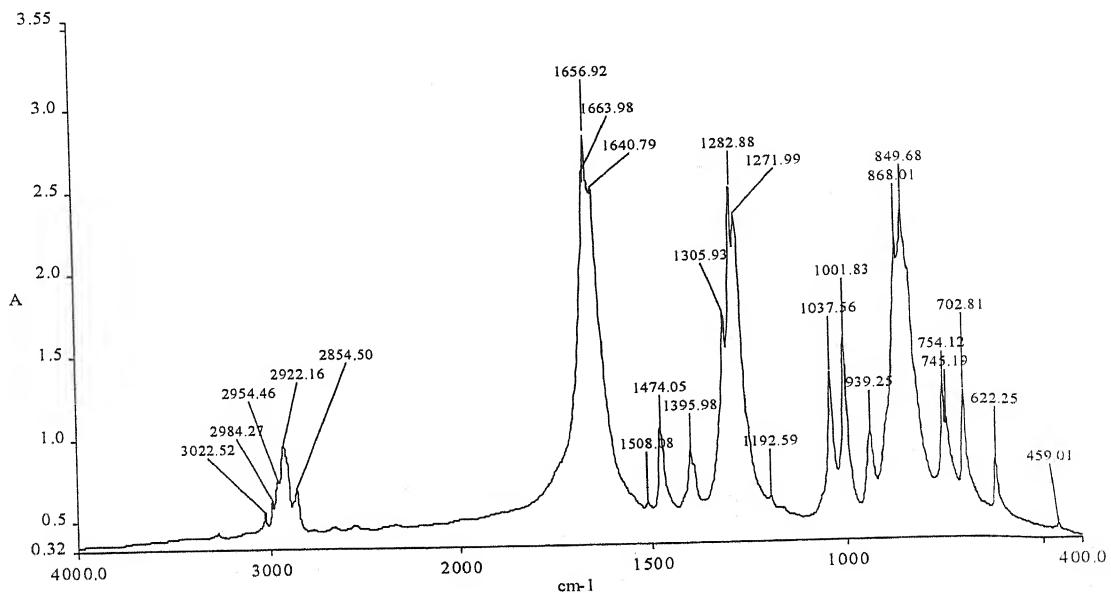
Fig.g.23-PETN + HSD
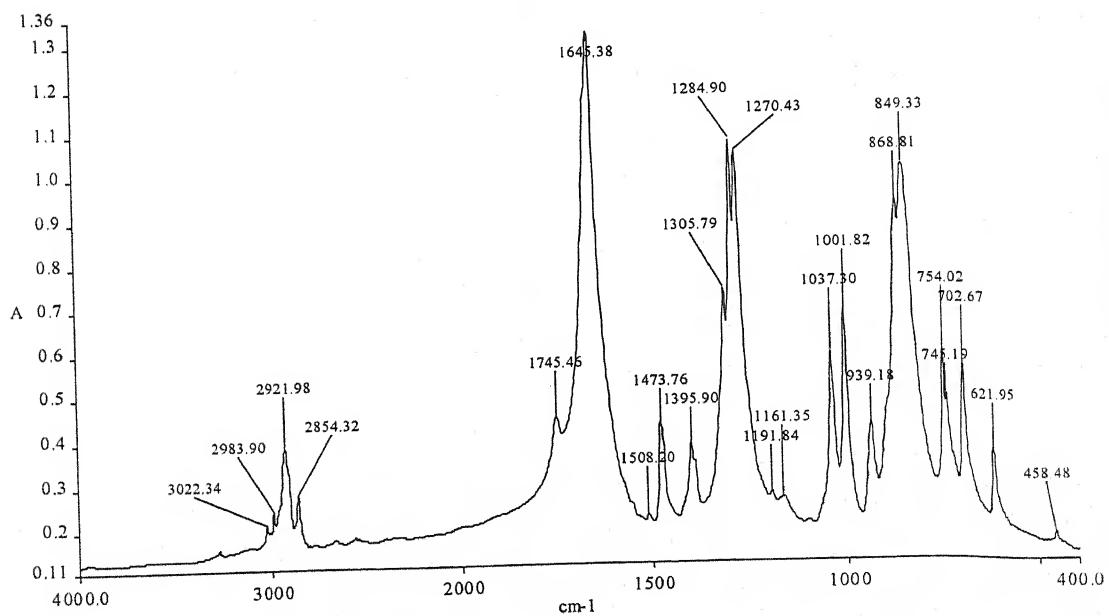

Fig.g.66-PETN + Mustard Oil
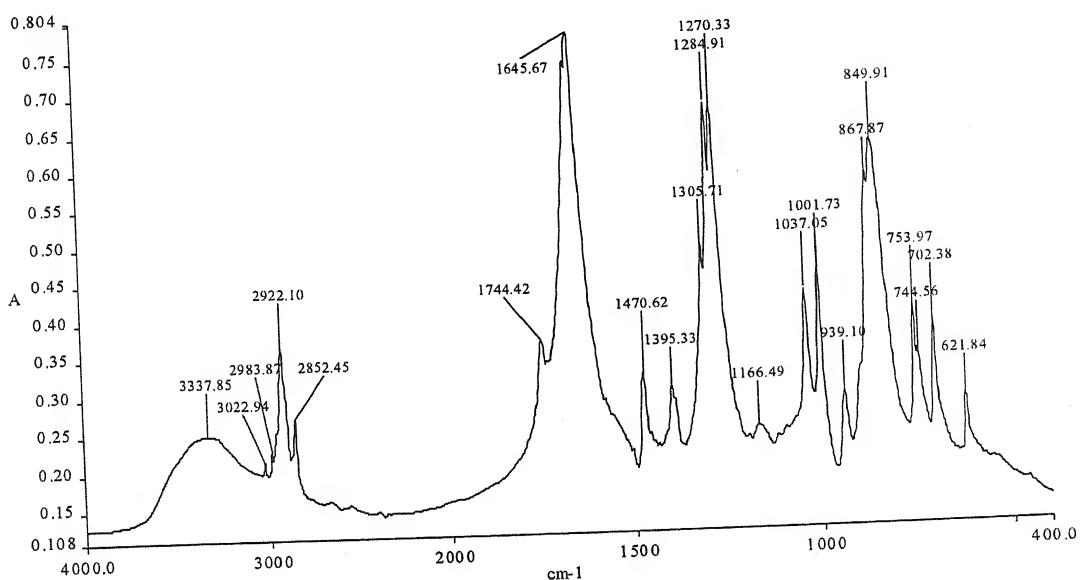
Fig.g.95-PETN + Milk Concentrate

TABLE-9

(All peak values rounded off to near digit)

PETN+HSD (cm⁻¹)	PETN (cm⁻¹)	HSD (cm⁻¹)
3023	3023	
2985	2984	
2955		2955
2922		2924
	2907	
2854		2854
1657	1656	
1664		
1641	1644	
		1605*

1474	1474	
		1460*
1396	1396	
		1377*
1306	1306	
1283	1284	
1272	1270	
1193		
1038	1037	
1002	1002	
939	939	
868	867	
850	848	
		810*
754	754	
		722*
745	745	
703	703	
622	623	
459		

TABLE-10

(All peak values rounded off to near digit)

PETN+ Mustard oil (cm^{-1})	PETN (cm^{-1})	Mustard oil (cm^{-1})
3022	3023	

		3007
2984	2984	
2922		2924
	2907	
2854		2854
1746		1747
	1656	
1645	1644	
1508		
		1465
1474	1474	
		1418
1396	1396	
		1378
1306	1306	
1285	1284	
1270	1270	
		1237
1192		
1161		1163
		1119
		1100
1037	1037	
1002	1002	
		968
939	939	
869	867	

849	848	
754	754	
745	745	
		722
703	703	
622	623	
458		

MIXTURES OF RDX WITH DIFFERENT SUBSTANCES:

In the case of RDX, the first spectrum examined is that of mixture of RDX with paraffin oil (fig.g.35) in the ratio of 9:1. The absorption peaks (cm^{-1}) of the mixture are identified to their source of RDX (fig.f.4) and paraffin oil (fig.a.2) as stated in Table-11.

Absorption peaks due to paraffin oil are present at 2923 cm^{-1} and 2854 cm^{-1} in the spectrum of mixture of RDX and paraffin oil. Split band comprising two peaks at 2930 cm^{-1} and 2915 cm^{-1} representing paraffin oil fig.a.2 has appeared as a merged peak at 2923 cm^{-1} in the spectrum of mixture of RDX and paraffin oil. Three peaks present in paraffin oil at 1305 cm^{-1} (ωCH_2), 1155cm^{-1} (τCH_2) and 722 (ρCH_2) have been obscured by the strong absorption bands produced by RDX in these regions. It is interesting to observe the absorption spectrum of mixture of RDX and paraffin oil. In spite of the fact that paraffin oil is present in the RDX, then even all the absorption peaks representing RDX can be seen in the Infrared spectrum of

mixture of RDX and paraffin oil. Absorption peak of RDX at $3001cm^{-1}$ seen in the spectrum of pure RDX has also appeared as a sharp peak in the spectra of combine RDX and paraffin oil. Same pattern of absorption peaks in the spectra has been observed with mixtures formed with RDX and other petroleum products taken for this study (g.34 to g.44).

One substance of vegetable origin has been taken for examination of the nature of spectrum created by its mixture with RDX. Absorption peaks (cm^{-1}) of RDX + Vegetable fat (fig.g.80), RDX (fig.f.4) and Vegetable fat (fig. b.9) are given in Table-12.

In the spectrum of mixture of RDX + Vegetable fat, absorption peaks at $2923cm^{-1}$ ($v_{as}CH2$), 2853 cm^{-1} (v_sCH_2) and 1747 cm^{-1} ($vC=O$) representing vegetable fat can only be seen. Remaining all peaks characteristic to vegetable fat including those, which represents triglyceride, have been masked by strong absorption bands produced by RDX. Absorption peak representing Unsaturation in the vegetable fat appearing at 3006 cm^{-1} has also appeared as a shoulder with the peak at 2923 cm^{-1} in the spectrum of mixture of RDX and vegetable fat. One of the factors, which contribute for the non-detection of the absorption peaks representing vegetable fat, is also that the concentration of vegetable fat in the mixture has been reduced to 10%, which has also resulted in their low absorption intensity. On the other hand, all absorption bands representing RDX including even the weaker one can be clearly seen in the spectrum of

mixture of RDX and vegetable fat. It is another matter that the concentration of RDX in the mixture, which is 90%, does not allow the masking of any peak of RDX by absorption peaks representing vegetable fat. In brief, absorption peaks of RDX in combination with approximately 10% vegetable fat stand clearly identified in its spectrum. Hence, it is very easy to identify RDX within shortest possible time in such mixtures. Same pattern of spectra is given by RDX in mixtures with other vegetable oils (g.72 to g.80) including that of animal origin such as lard (g.84), honey bee wax (g.88), milk fat (g.92) and milk concentrate (fig.g.96). The indication of castor oil among the vegetable oils could be seen due to the reason that secondary alcoholic group present in the ricinoleic acid, a major constituent of castor oil, produces a strong absorption band in the form of hump at 3350 cm^{-1}. Similarly, the spectrum of mixture of RDX with Milk concentrate (fig.g.96) is also very peculiar. Absorption peaks of milk concentrate are present in plenty in the spectrum of mixture of RDX and milk concentrate such as strong absorption hump at about 3368 cm^{-1}, 2954 cm^{-1}, 2922 cm^{-1}, 2870 cm^{-1}, 2853 cm^{-1}, 1744 cm^{-1}, 1651cm^{-1}, 1644 cm^{-1}, 1634 cm^{-1}, 1558 cm^{-1}, 1168 cm^{-1}, 1117 cm^{-1}, 1094 cm^{-1} and 1073 cm^{-1}. In spite of the presence of numerous peaks representing milk concentrate in the spectrum of mixture of RDX and milk concentrate; plenty of absorption bands of RDX are present in the spectrum of mixture of RDX and milk concentrate. Hence, in spite of the fact that both the substances forming the mixture are

producing many peaks representing milk concentrate and RDX, it is possible to identify RDX in such a mixture including an indication of milk concentrate added as a moulding agent.
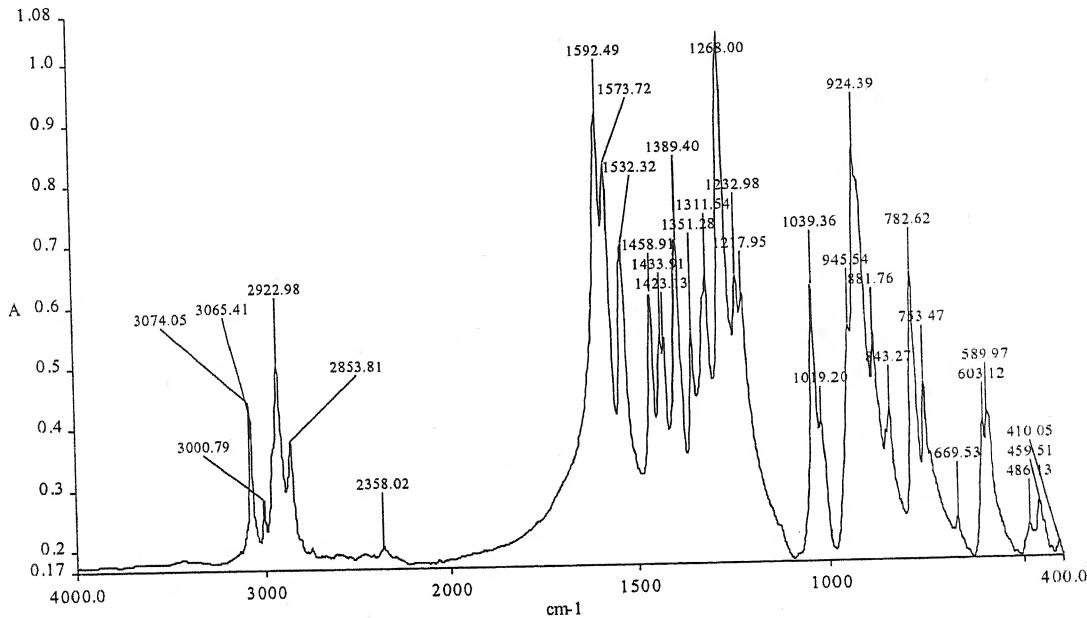

Fig.g.35-RDX + Paraffin Oil
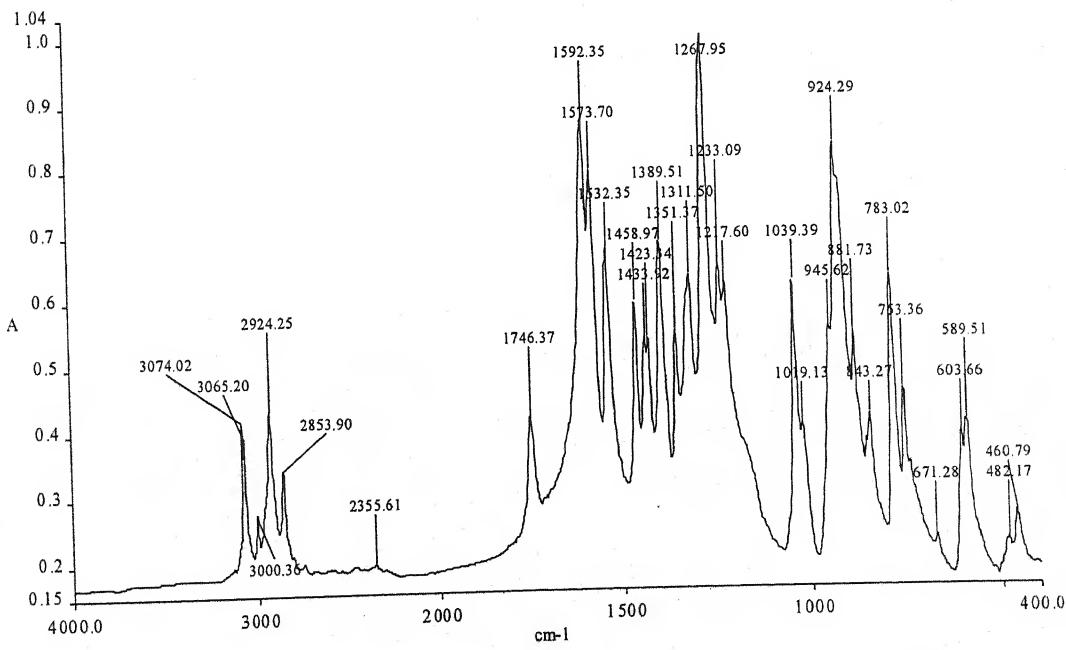
Fig.g.80-RDX + Vegetable Fat
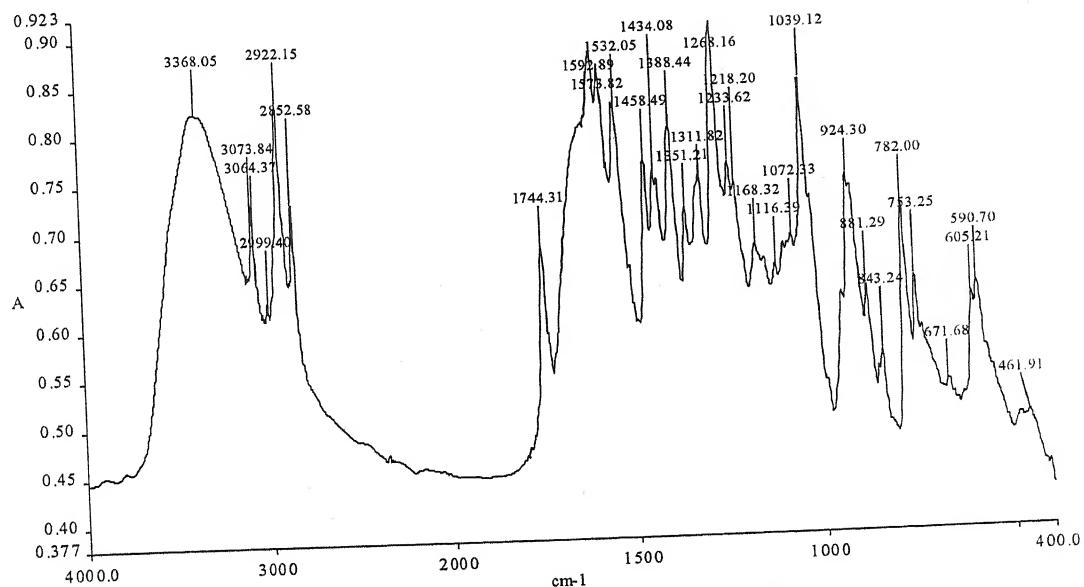
Fig.g.96-RDX + Milk concentrates

TABLE-11

(All peak values rounded off to near digit)

RDX + Paraffin oil (cm⁻¹)	RDX (cm⁻¹)	Paraffin oil (cm⁻¹)
3074	3074	
3065	3065	
3001	3001	
		2956
		2930
2923		
		2915
2854		2854
1593	1592	
1574	1573	
1532	1533	

1459	1459	1460
1434	1434	
1423	1423	
1389	1389	
		1377
1351	1351	
1312	1312	
		1305
1268	1267	
1233	1233	
1218	1217	
		1155
1039	1039	
1019	1019	
946	945	
924	924	
882	881	
843	842	
783	782	
753	753	
	739	
		722*
670	670	
603	603	
589	589	
	485	
479		
459	459	

TABLE-12

(All peak values rounded off to near digit)

RDX + Vegetable fat(cm⁻¹)	RDX (cm⁻¹)	Vegetable fat (cm⁻¹)
3074	3074	
3065	3065	
		3005
3000	3001	
2923		2922
2853		2854
1746		1747
1592	1592	
1574	1573	
1532	1533	
		1465
1459	1459	
1434	1434	
1423	1423	
		1418
1389	1389	
		1378
1351	1351	
1312	1312	
1268	1267	
		1236
1233	1233	

1218	1217	
		1163
		1119
		1099
1039	1039	
1019	1019	
		967
946	945	
924	924	
882	881	
843	842	
782	782	
753	753	
	739	
		722
671	670	
604	603	
590	589	
482	485	
460	459	

MIXTURES OF EXPLOSIVE SUBSTANCES WITH SUGARS /STARCHES & OILS:

Another type of improvised mixtures of organic explosives has been encountered in a case, where starch mixed with a petroleum product was used as a moulding agent for explosive substance PETN. The quantity of

explosive substance has been found to be approximately 70%. The experiments were conducted for recording spectra of mixtures of sugars/starches mixed with oils of petroleum, vegetable and animal origin in just enough quantity so as to convert TNT, CE, PETN and RDX into a mouldable mixture. It was observed that about 10% of starch/sugar with 20% of the oil mixed with explosive substance is an appropriate mixture. However, such mixtures were prepared by keeping the quantities of explosive substance, oil and sugar / starch in a ratio of 2:1:1. It has been done so as to see whether in spectra of such mixtures, where the quantity of explosive substance has been reduced, the identification of explosive is possible or not? Spectra of these samples marked as g.97 to g.120 were recorded. Selected spectra of TNT, CE, PETN and RDX forming a mixture with brown sugar and engine oil are shown in figureg.97 to g.100. Similarly, spectra of the explosive mixtures with starch and cottonseed oil are shown in figure g.113 to g.116. In these mixtures also, characteristic absorption bands due to Methylene antisymmetric and symmetric stretching can be seen. Further, typical absorption bands due to Carbonyl group, Triglycerides and extended chains comprising repeated methylene groups could also be sensed from the spectra of the mixtures. From the spectra of these mixtures, it became difficult to get any indication about the nature of the sugar or starch. However, the presence of 50% material comprising sugar/starch and oils mixed, as a moulding agent, could not suppress

detection of explosive substances. The explosive substance down to 50% level in presence of above stated moulding agents could be detected from the numerous strong and weak absorption bands linking to the structure of the explosive substances. Even the library search in spectra of such mixtures could provide maximum probability of the match with the correct identification of the explosive substance.
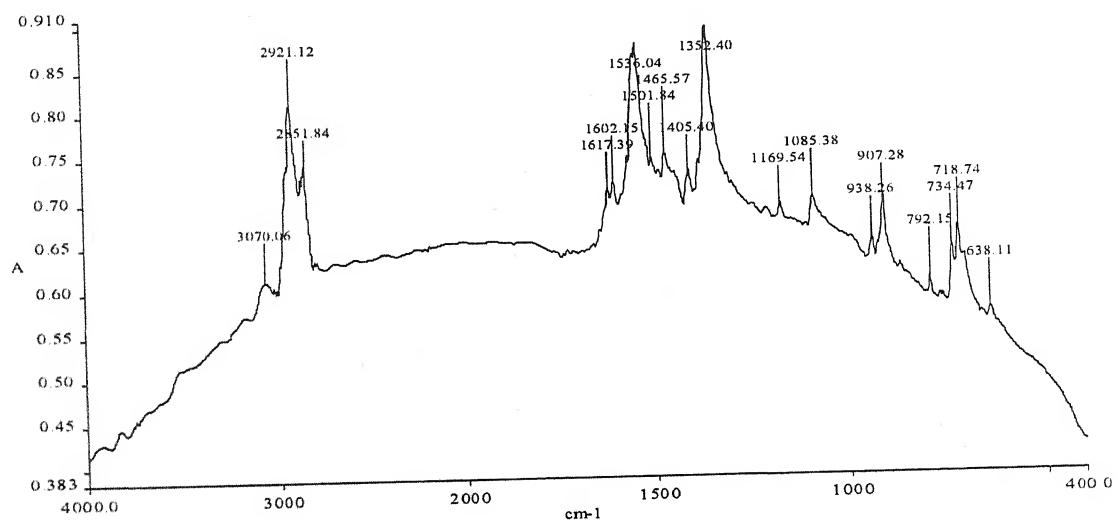

Fig.g.97-TNT + Engine Oil and Shakkar
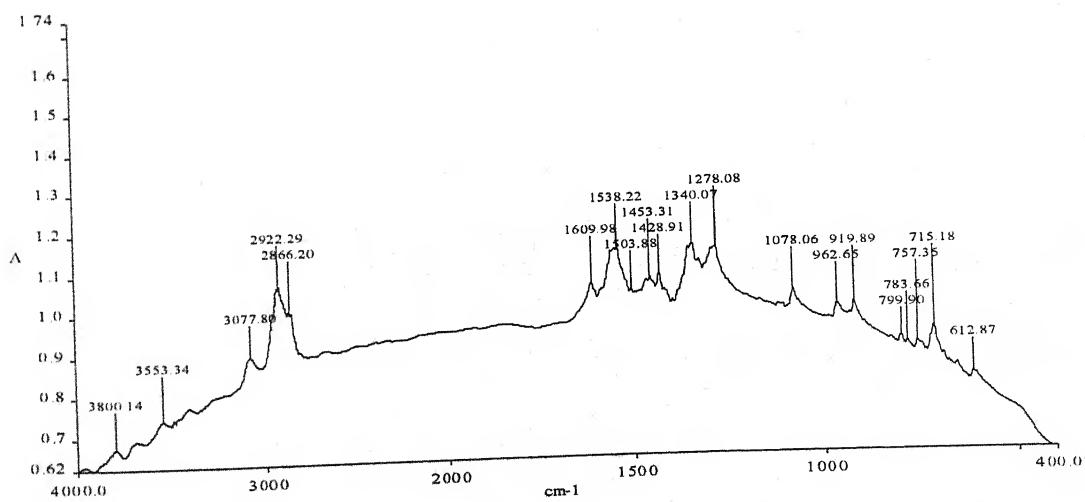
Fig.g.98-CE + Engine Oil and Shakkar
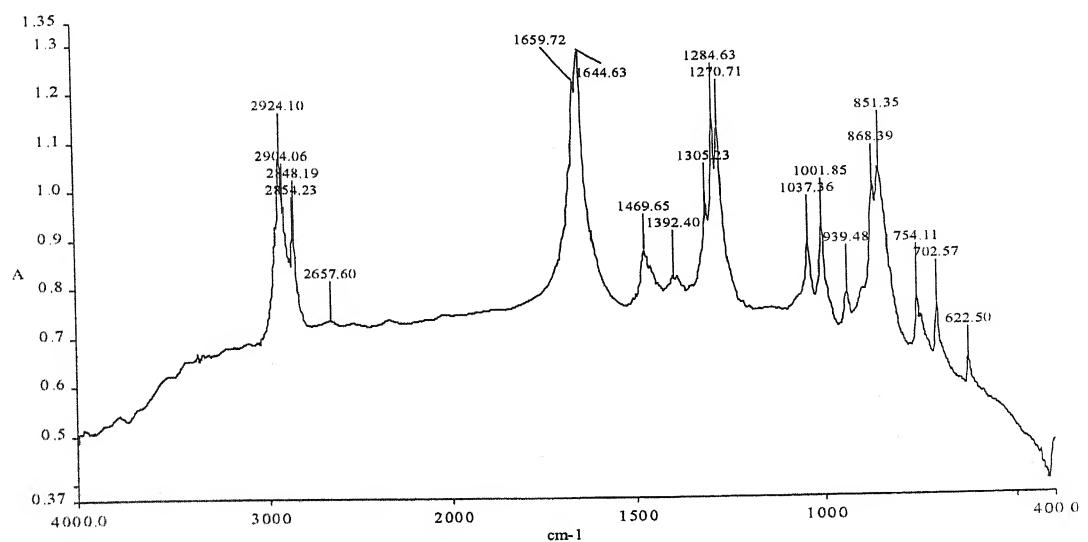
Fig.g.99-PETN + Engine Oil and Shakkar
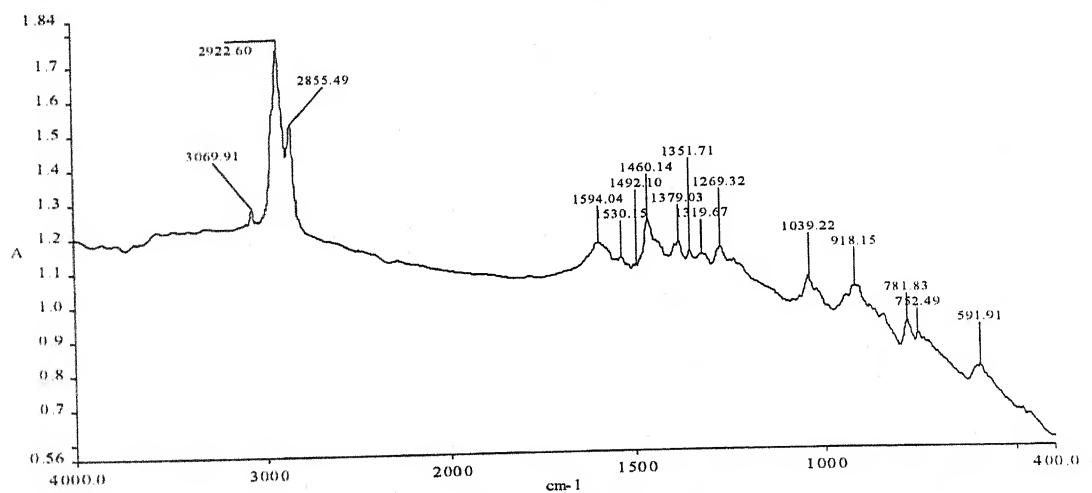
Fig.g.100-RDX + Engine Oil and Shakkar
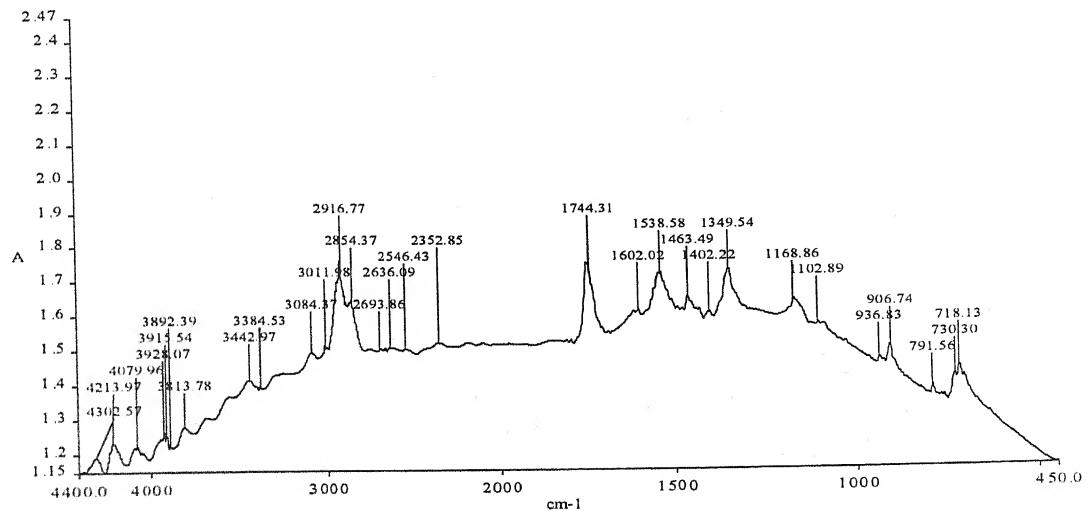
Fig.g.113-TNT + Cottonseed Oil and Starch
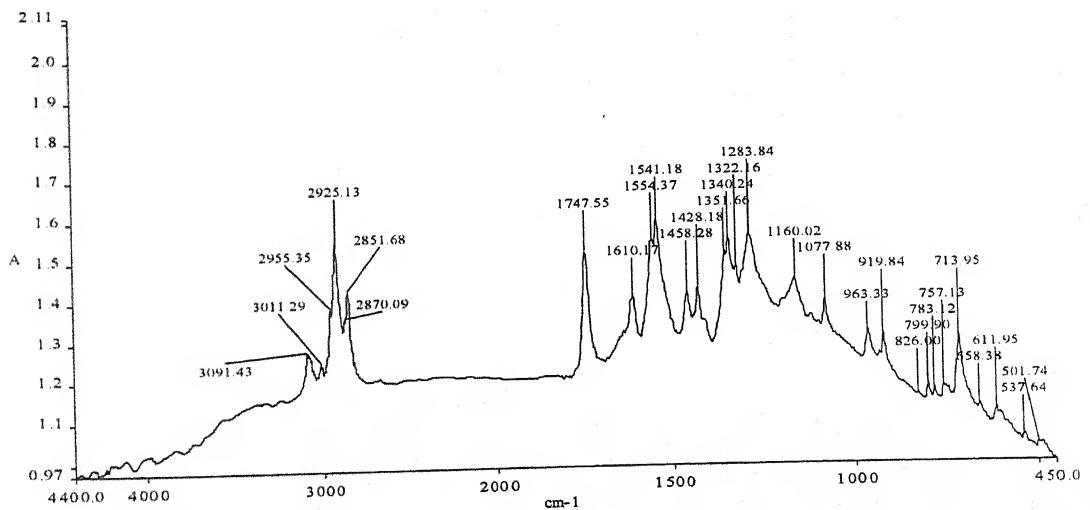
Fig.g.114- CE + Cottonseed Oil and Starch
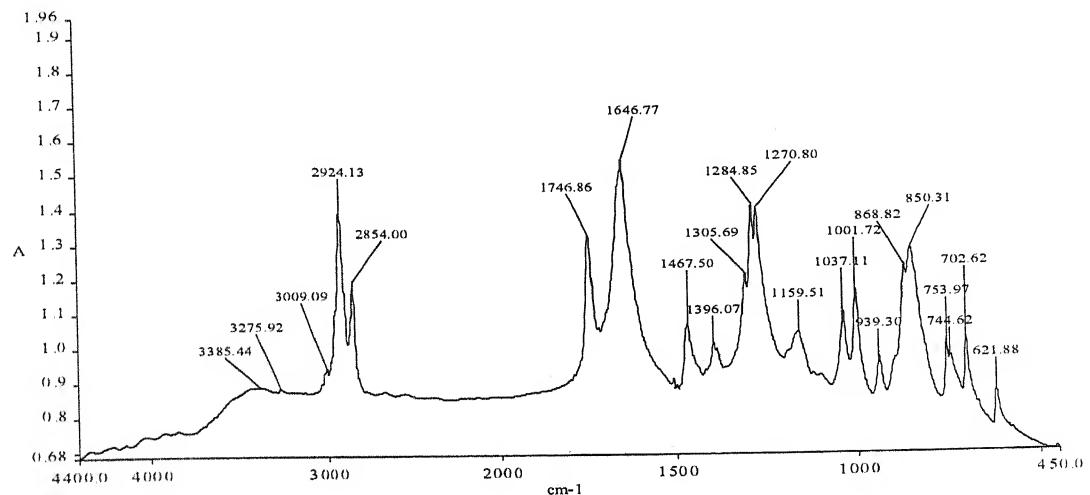
Fig.g.115- PETN + Cottonseed Oil and Starch
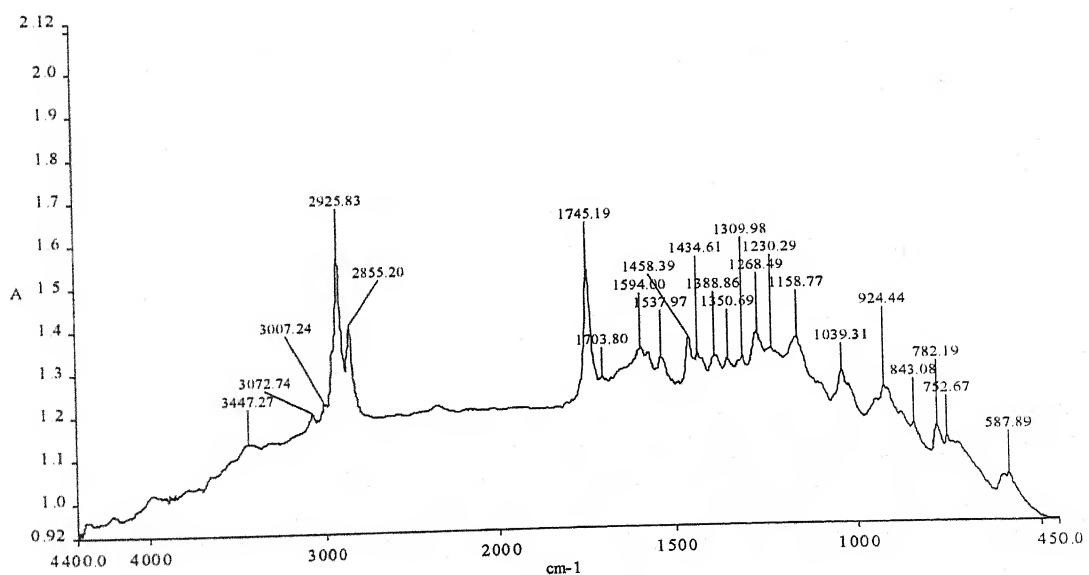
Fig.g.116- RDX+ Cottonseed Oil and Starch

POST BLAST SAMPLES

Spectrum of all four explosives substances can be seen in fig.1. Initial recording of sample was done with enough concentration so that absorption bands can be seen conspicuously. It is evident that there are many strong or medium type absorption bands in spectrum of each substance which are characteristic. Two absorption bands at $1537cm^{-1}$ and $1353\ cm^{-1}$ are strongest peaks in spectrum of TNT indicating its nitro groups. There is structural similarity in between TNT and CE except the substitution of $-CH_3$ in TNT and NO_2NCH_3 for CE. For CE these bands appear at $1542\ cm^{-1}$ alongwith a shoulder at $1556\ cm^{-1}$ and another band with split peaks at $1340\ cm^{-1}$ and $1284\ cm^{-1}$ with shoulders at $1352\ cm^{-1}$ and $1323\ cm^{-1}$. In fact, absorption band at $1284\ cm^{-1}$ indicates presence of N-N band in Tetryl. Similarly in spectrum of both TNT and CE there are plenty absorption bands in range $700\ cm^{-1}$ to $800\ cm^{-1}$ representing quadruple substitutions. PETN spectrum contained bands at $1646\ cm^{-1}(s)$, where none of other three substances show any peak. Same substance is producing strong absorption bands at $1285\ cm^{-1}$ and $1271\ cm^{-1}$, $868\ cm^{-1}$ and $850\ cm^{-1}$ and at $745\ cm^{-1}$ & $754\ cm^{-1}$ in doublets. Similar doublets at 1593 and 1573 cm^{-1}, $603\ cm^{-1}$ and $590\ cm^{-1}$ become characteristic of RDX. Hence, in spite of similarity in containing 3 to 4 nitro groups in each substance, absorption bands in range of IR spectrum appeared at different wave numbers either singlet or doublets due to difference of structural environment. Spectrum of

vegetable oils and oils of petroleum origin contain bands which also can give the indication of their presence alongwith any of the explosive substance formulations, either exploded or unexploded. Strong absorption band at $1745cm^{-1}$ and a triplet at $1236\ cm^{-1}$, $1163\ cm^{-1}$ and $1119\ cm^{-1}$ indicates oils of vegetable origin. On the other, hand greases and lubricating oils added to improvise organic explosive formulations behave like nujol used in recording IR spectrum of many substances. Strong absorption band in area around $2922\ cm^{-1}$, $2856\ cm^{-1}$ and $2955\ cm^{-1}$ indicates C-H stretching bands of petroleum products. Even vegetable oils show these bands but the other band at $1745\ cm^{-1}$ due to CO group and triplet around $1163\ cm^{-1}$ represents triglycerides produce the difference in spectrum due to structural difference in both type of oils (fig.2-3). Expansion of x & y- axis of spectrum shows more vivid picture of location of small absorption bands. This facility suits more to understand mixtures of explosive substances containing moulding agents, which in such mixtures have been found to be not more than quarter of the total bulk. In fact, it is added to about 15% of the total amount of bulk, otherwise the power of explosion due to inclusion of non-explosive substance will be reduced.

Originally a sample of explosive substance with Potassium bromide was prepared in ratio of 1:100. Only 50 mg of this sample mixture was palletized to record first spectrum. The remaining mixture was diluted further with Potassium bromide to measure minimum detection limit of each

substance. The amount used in penultimate recording or last but one recording was treated as minimum detection limit of any explosive substance because in ultimate experiment there will be flat absorption line without any characteristic band showing explosive substance. Hence, minimum detection limit was found to be about 2 micrograms of each explosive substance (Fig.4-7), to be palletized with 50 mg Potassium bromide.

For analysis with GC, GC-MS, LC or LC-MS also certain minimum amount of solution of explosive substance is required for its injection into the instrument with syringe or auto sampler. Sample solution should be well filtered devoid of particulate matter otherwise it will chock syringe, can create obstruction in narrow flow line of auto sampler/LC. In fact, quantity of substance which can be analyzed by these instruments is of the order of nanogram range. However, to handle such samples in solution form before injection, about a millilitre of solution required. Thus, amount of substance required also will be of the order of a few micrograms. Thus, with the above experiment with IR spectrophotometer, also a few microgram of substance is enough for their correct identification. On the other hand, advantage of FTIR spectrophotometer is that it is totally a non-destructive technique. Extraction of explosive substance from potassium bromide pellet involved treatment with a few micro litres of acetone solvent.
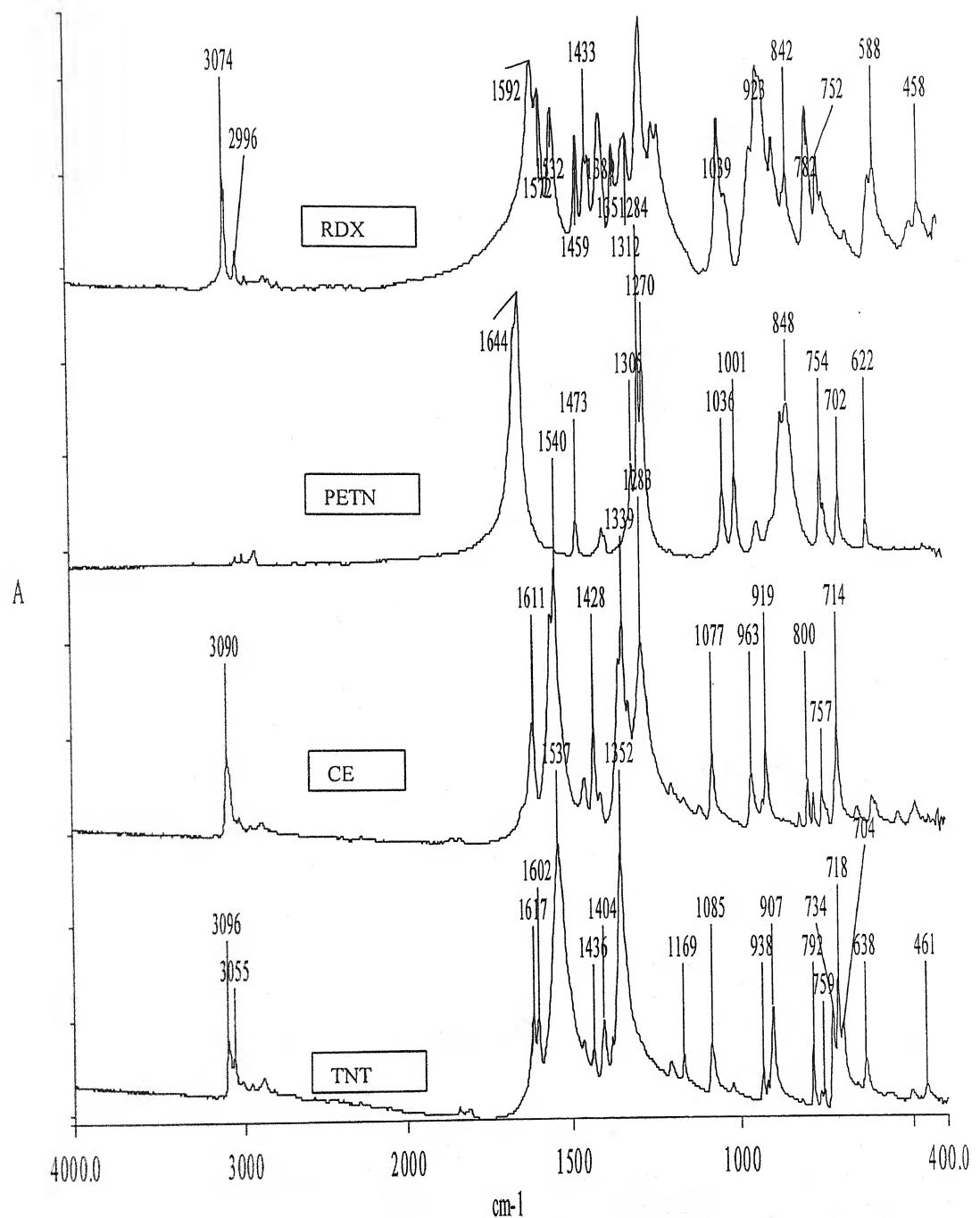
Fig.1 Spectra of Standard Explosives (TNT, CE, PETN & RDX)
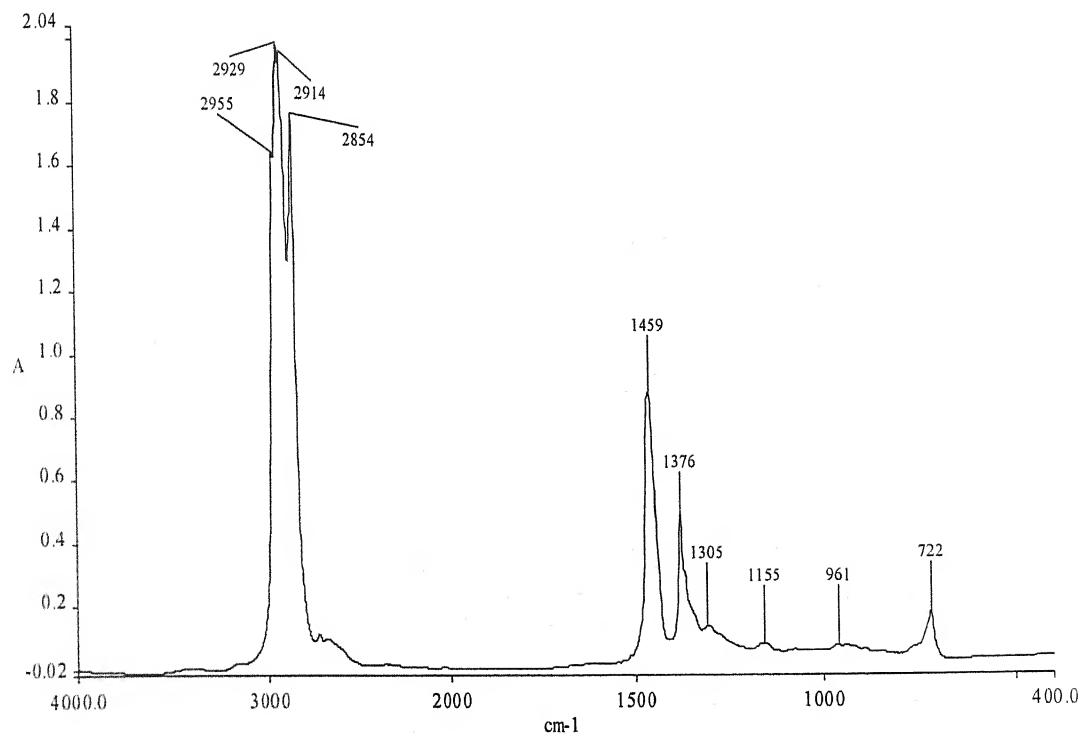
Fig.-2 Oil of Petroleum origin
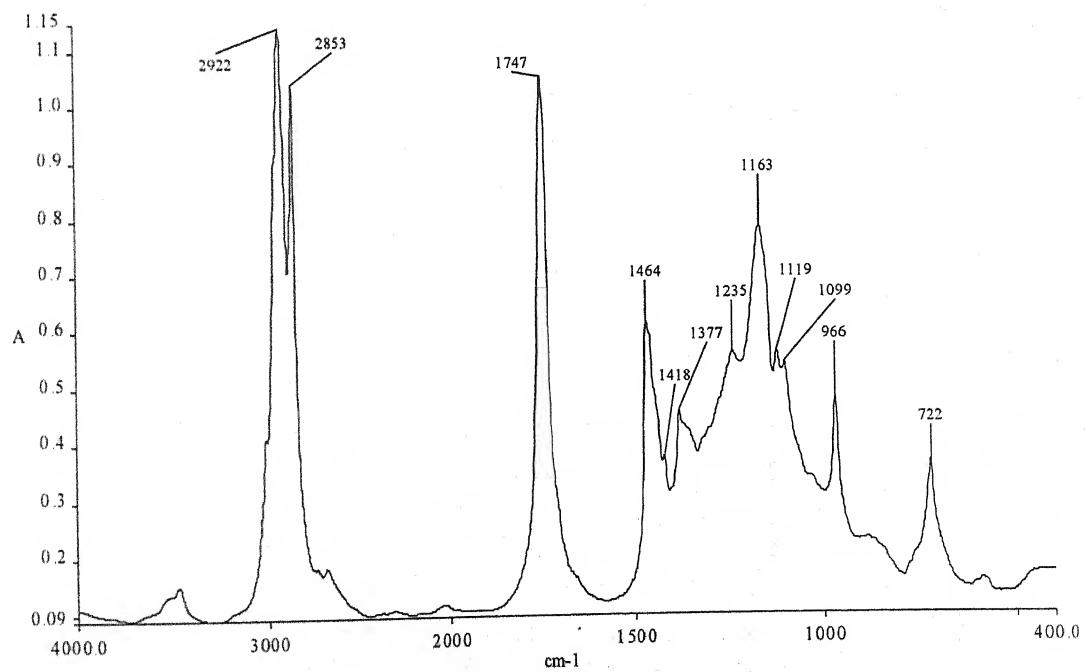

Fig.-3 Oil of Vegetable origin
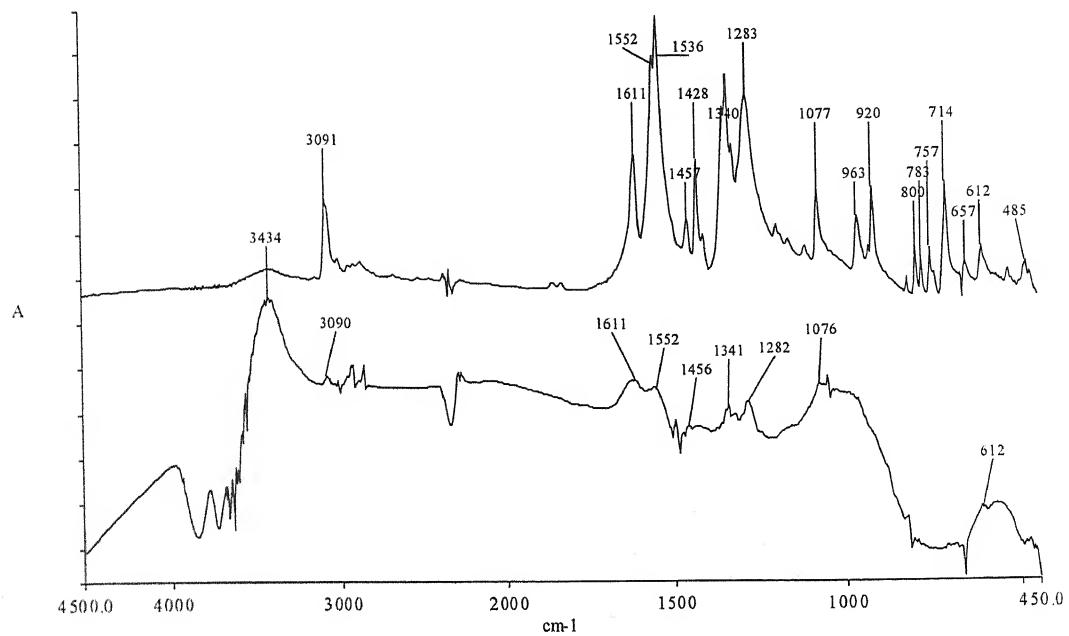
Fig.-4 TNT (concentrations 1 mg. and 2 mcg.)
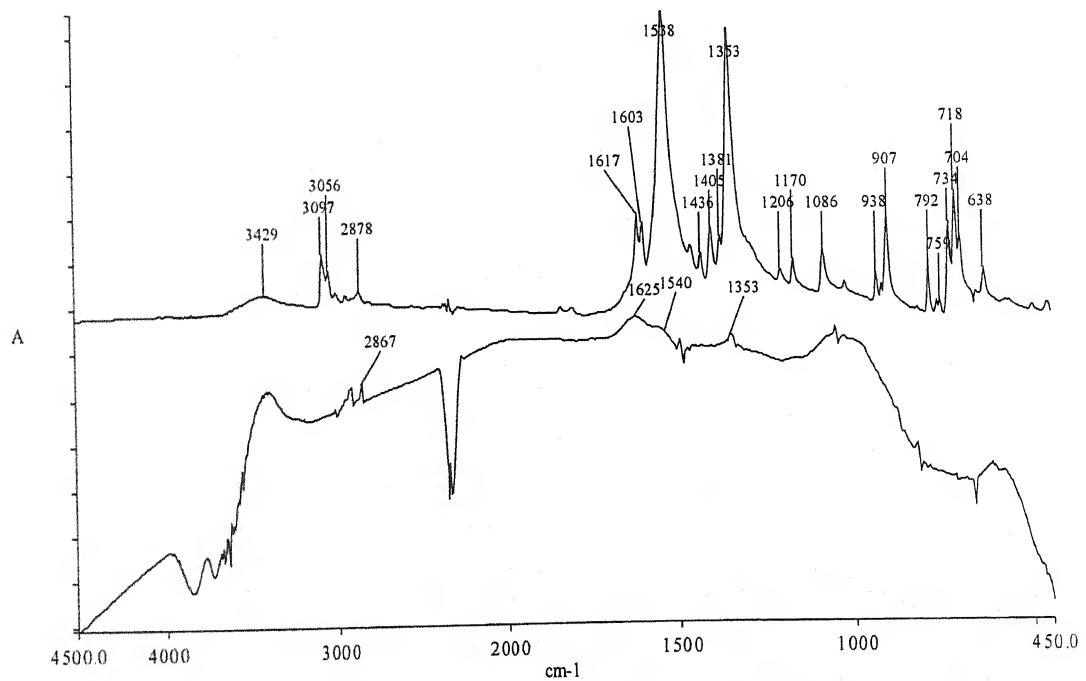
Fig.-5 CE (concentrations 1 mg. and 2 mcg.)
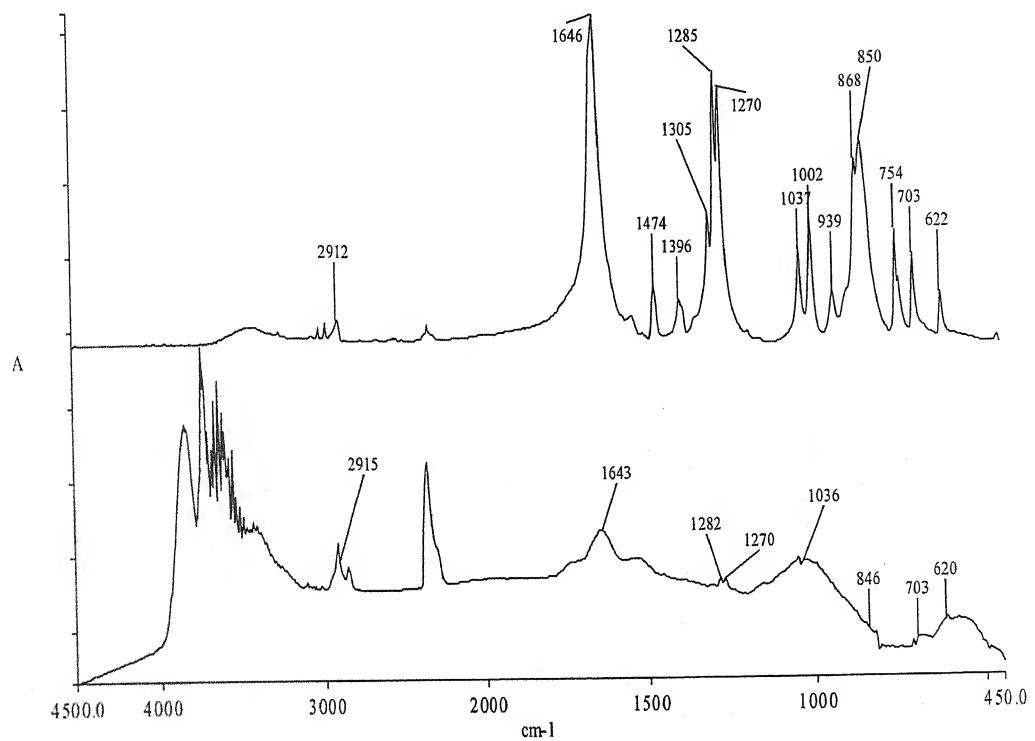
Fig.6 PETN (concentrations 1 mg. and 2 mcg.)
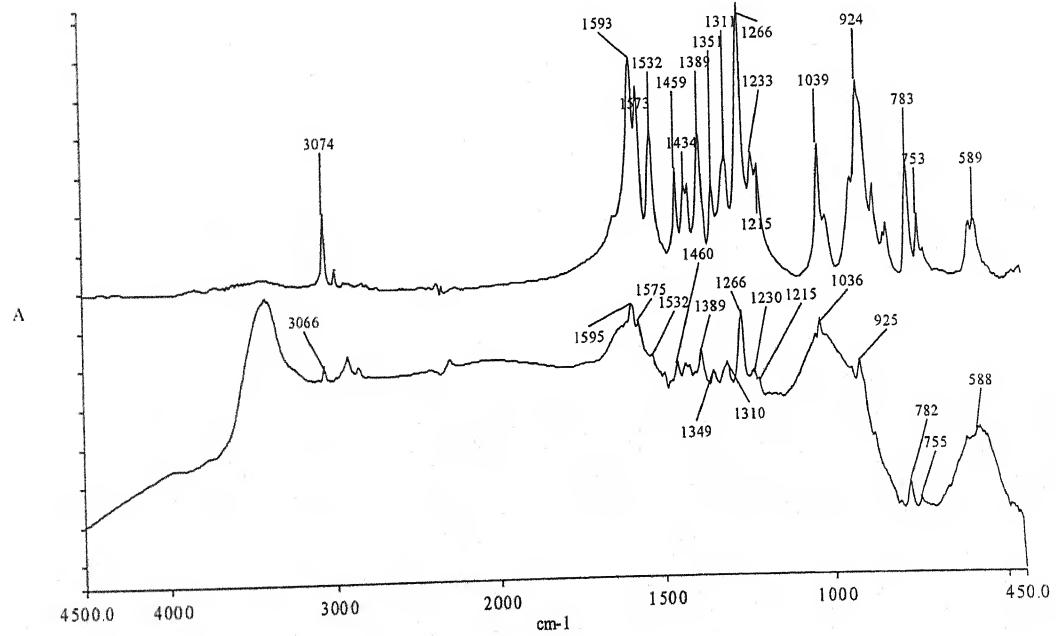
Fig.-7 RDX (concentrations 1 mg. and 2 mcg.)
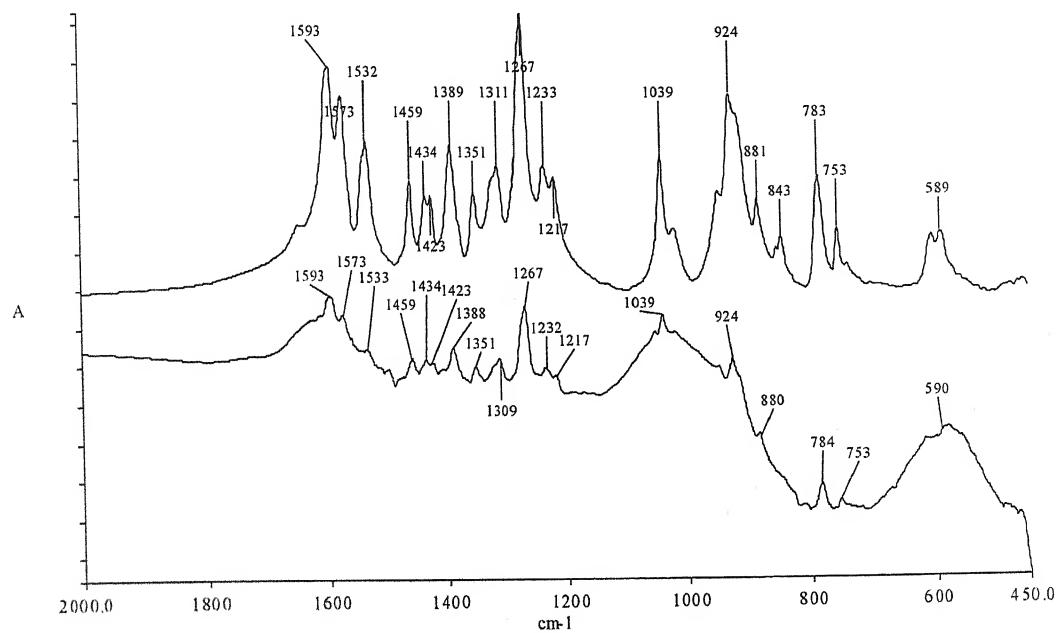
Fig.7a RDX (concentrations 1 mg. and 2 mcg.) with x-axis expansion

Chapter-5

ANALYSIS OF CASE SAMPLES (FORMULATIONS & POST BLAST)

Some explosive formulations seized by the police authorities, intended to be used for committing criminal activities, have been analysed by FT-IR Spectrophotometric technique. Explosive substances have been manipulated and shaped suitably for their use in improvised explosive devices. About one milligram of the suspect substance was pulverised with about one hundred milligram of potassium bromide and its pellet was prepared for recording spectrum. Library match was carried out for the identification of the explosive substance. All absorption peaks in the spectra of the mixtures were scanned to get an indication of the explosive substance and modifying agents mixed with the explosive substance for moulding into desired shape. Results of analysis of some seized formulations have been described as given below:

1. JAIL BREAK
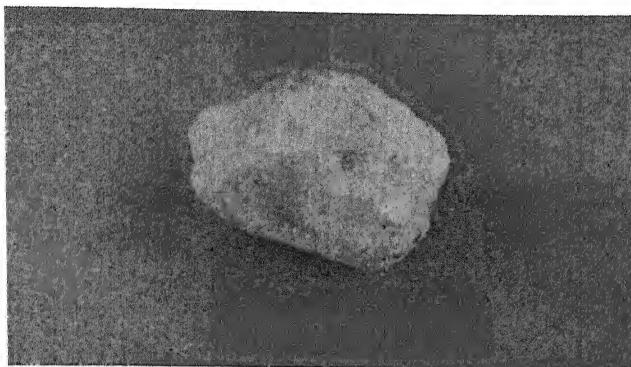
Explosive in the form of sweet

In a case an attempt was made to smuggle an Explosive substance shaped like an Indian Sweet into a jail. Spectrum of the sample is given in fig.h-1. It is showing all characteristic bands (cm^{-1}) of PETN at 3022, 2982, 1654, 1648, 1396, 1306, 1285, 1271, 1037, 1002, 939, 868, 849, 754, 744, 702 and 622. Only characteristic strong sharp absorption band seen in spectrum of PETN ((fig.f.3) at 1474 cm^{-1} has been found marked at 1467 cm^{-1} in fig.h.1 due to its flat shape. Another minor absorption band at 2907 cm^{-1} seen in spectrum of pure PETN (fig.f.3) has also been observed to merge with neighbouring band in the spectrum (fig.h.1) of the formulation. Bands at 2922 cm^{-1} and 2853 cm^{-1} are indicative of a substance comprising chain of repeated methylene units. Spectrum fig.h.1 is devoid of any absorption band near about 1746 cm^{-1} indicative of carbonyl stretching frequency. Hence, the material mixed with PETN to shape it as sweet can be oil of petroleum origin and certainly not of vegetable or animal origin. The spectrum could not indicate the presence of starch in the formulation. It

could have been detected from the residue left on the filter paper during the filtration of acetone solution of the sample.
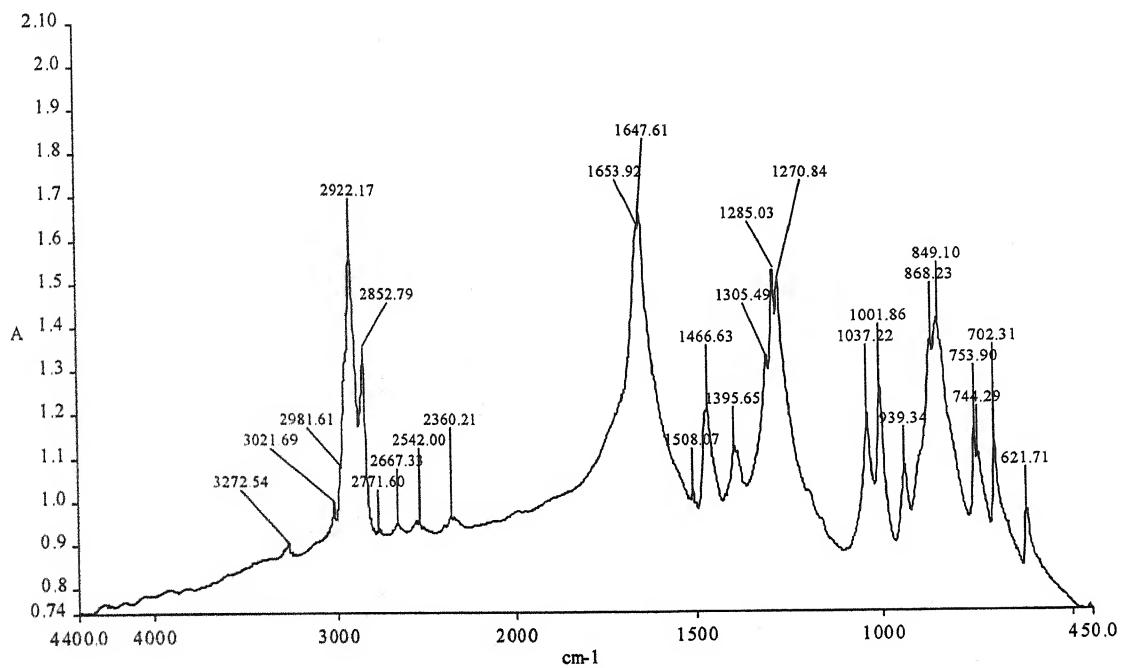

Fig.h.1- Spectrum of Jail Break Sample

2. GARLAND
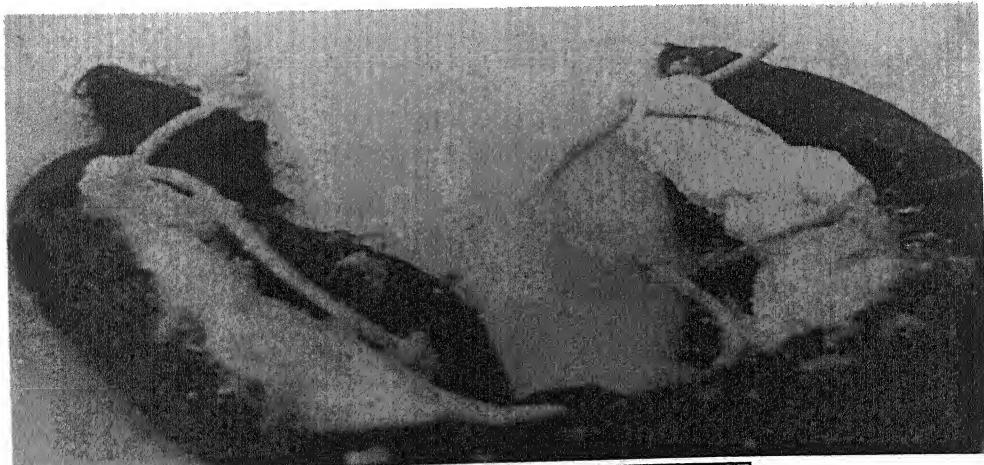
Garland base with explosive

About one kilogram of white material was wrapped around a detonating cord. It was further covered with a cloth piece and decorated with flowers to form a garland. Spectrum of the substance is given in

fig.h.2, from which explosive substance PETN could be identified. Absorption bands in spectrum fig.h.2 representing PETN, when compared with the bands in spectrum of pure PETN (Fig.f.3), were found to be quite accurate. It has been seen that the strong absorption bands at 2917 cm^{-1} and 2849 cm^{-1} in fig.h.2, have been found to match with absorption bands appearing at 2917 cm^{-1} and 2849 cm^{-1} as seen in the spectrum of wax figure a.10. Thus, from the spectrum fig.h.2, explosive substance PETN could be identified correctly. It certainly shows absence of oil / fat of plant or animal origin mixed with PETN. It indicates the additive mixed with PETN to be a substance like wax of petroleum origin. Thus, Infrared spectrum of the sample will also assist the forensic scientist to select a suitable technique to be used for characterisation of the moulding agent mixed with PETN.
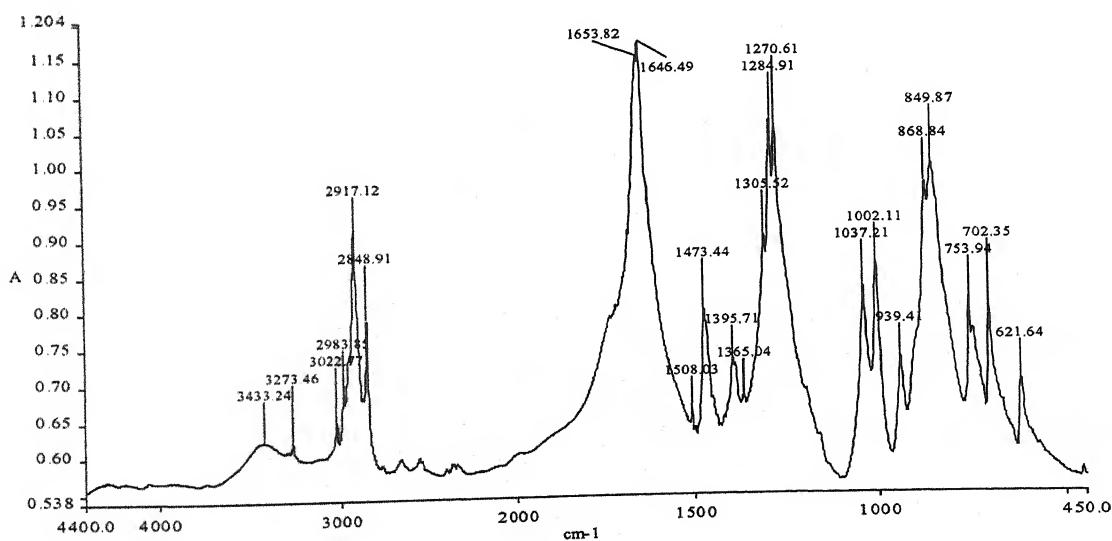

Fig.h.2- Spectrum of Garland material

3. MILKCAN
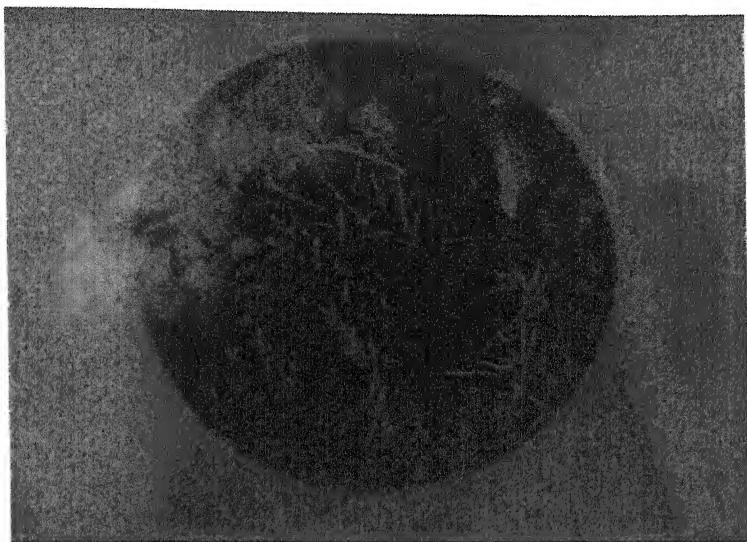
Milkcan with explosive & nails

This is another disguise, where milkcan have been used as an improvised explosive device. The material used to fill the milkcan on IR spectroscopic analysis produced a spectrum as given in figure h-3. Pattern of absorption bands (cm^{-1}) at 3074, 1571, 1458, 1437, 1423, 1389 ,1351, 1312, 1268 ,1233 1218, 1039, 1019, 947, 925, 882, 843, 784, 754, 670, and 603 is producing a library match of explosive substance RDX. Peaks at 2922 cm^{-1}, 2852 cm^{-1} and 1744 cm^{-1} are indicative of the additive to be a substance of vegetable or animal origin. Thus, in this case also, mere FT-IR spectrum of the sample could correctly characterise RDX in the mixture filled in the milkcan.
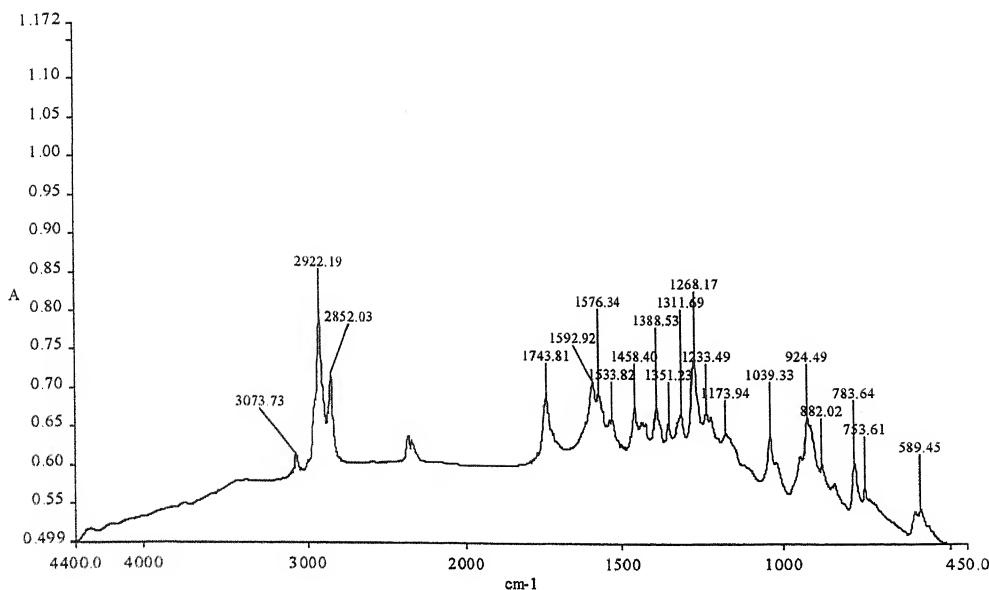
Fig.h.3- Spectrum of Milkcan material

4. TIFFIN BOX

A Tiffin Box filled with a lump of solid mass was recovered in another case. A hole was also made on one side of Tiffin for fitting an initiating device. Spectrum of the solid mass is as given in fig.h-4. From the absorption bands (cm^{-1}) in the spectrum figure h.4, there is no problem in identifying PETN in the mixture. Presence of absorption bands at 2956 cm^{-1}, 2926 cm^{-1} and 2850 cm^{-1} and absence of a band near 1746 cm^{-1} is indicative of the nature of the presence of moulding agent in the mixture filled in Tiffin Box to be of petroleum origin and not that of vegetable or animal origin.
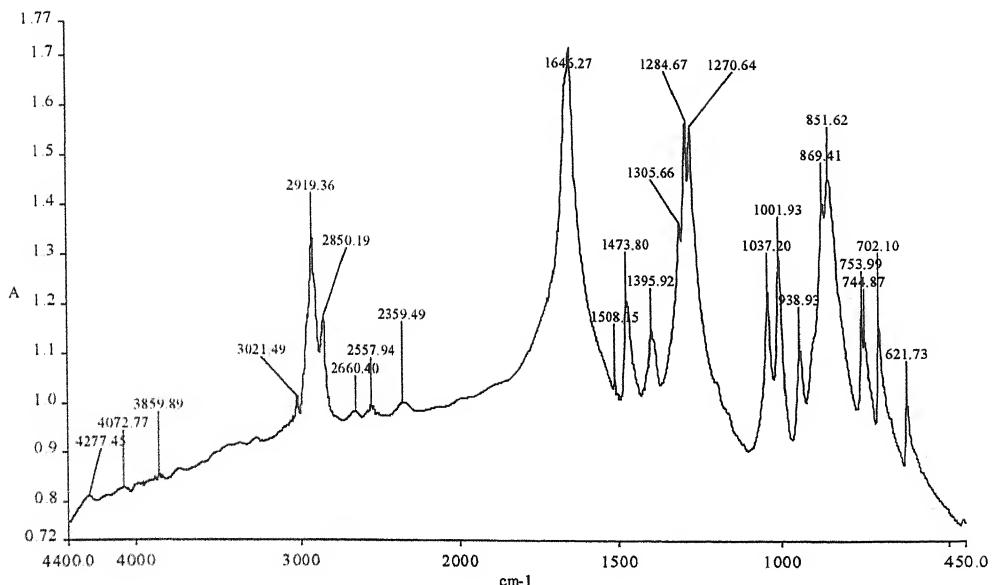
Fig.h.4- Spectrum of Tiffin Box material

5. YELLOW BRICK

In another case, sample in the form of a pale yellow brick with a round hole in the middle fitted with a distinct brown coloured solid plug was recovered. Spectra of both yellow and brown substances were recorded separately which are given in figures h.5a and h.5b. Spectra of yellow and brown coloured substances produced a perfect match with the spectra of TNT (fig.f.1) and Tetryl (fig.f.2) respectively. There is no extra characteristic absorption bands in spectra figures h.5a and fig.h.5b, which could indicate the presence of moulding agent used in both the samples in the present case.
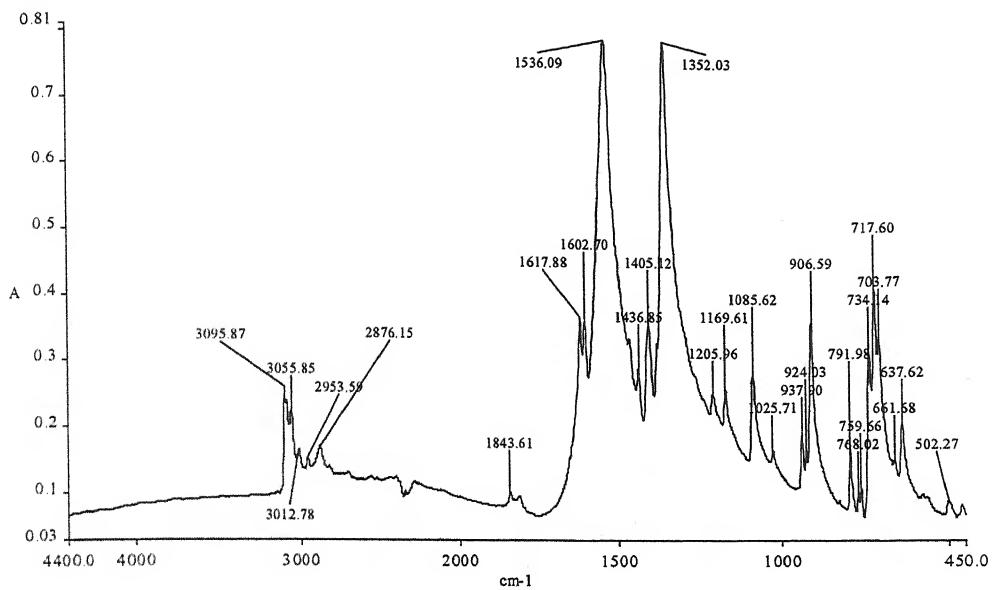
Fig.h.5a- Spectrum of Yellow Brick
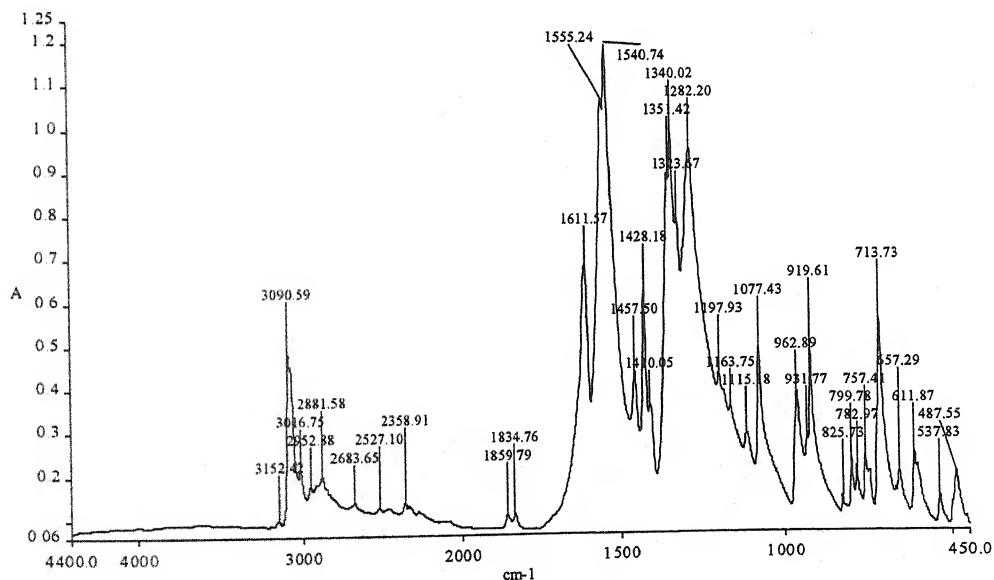
Fig.h.5b- Spectrum of Brown Plug

6. DRUG SAMPLE
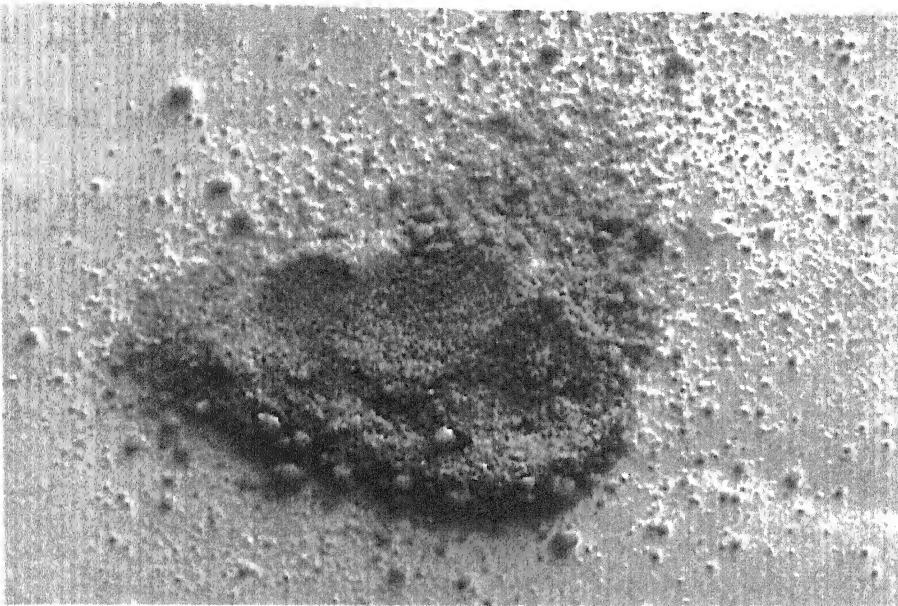
Drug sample

Police got secret information regarding trafficking of some banned drugs. A person was caught with about 20 Kg. brown coloured powder. It was revealed by the suspect that the material under reference was Indian country made sugar termed as Shakkar. However, police suspected the same to be brown sugar, a form of street heroin. A sample was sent to laboratory for identification. FT-IR Spectrophotometry, a quick and convenient technique to provide fingerprint identification was also attempted with this sample. Spectrum of the substance is given in fig.h.6, which matched with spectrum of high explosive PETN. Absorption bands at 2923 cm^{-1}, 2853 cm^{-1} and 2983 cm^{-1} are indication of a substance comprising chain of repeated methylene units. Spectrum is also devoid of absorption bands indicative of carbonyl group and also other bands

representing triglycerides moiety in the structure i.e. 1746 cm^{-1} and triplet in between 1100-1240 cm^{-1}. Hence, the material mixed with PETN can be oil of petroleum origin and certainly not of vegetable or animal origin. Thus, from the spectrum fig.h.6, explosive substance PETN could be identified correctly. It certainly shows absence of oil / fat of plant or animal origin mixed with PETN.
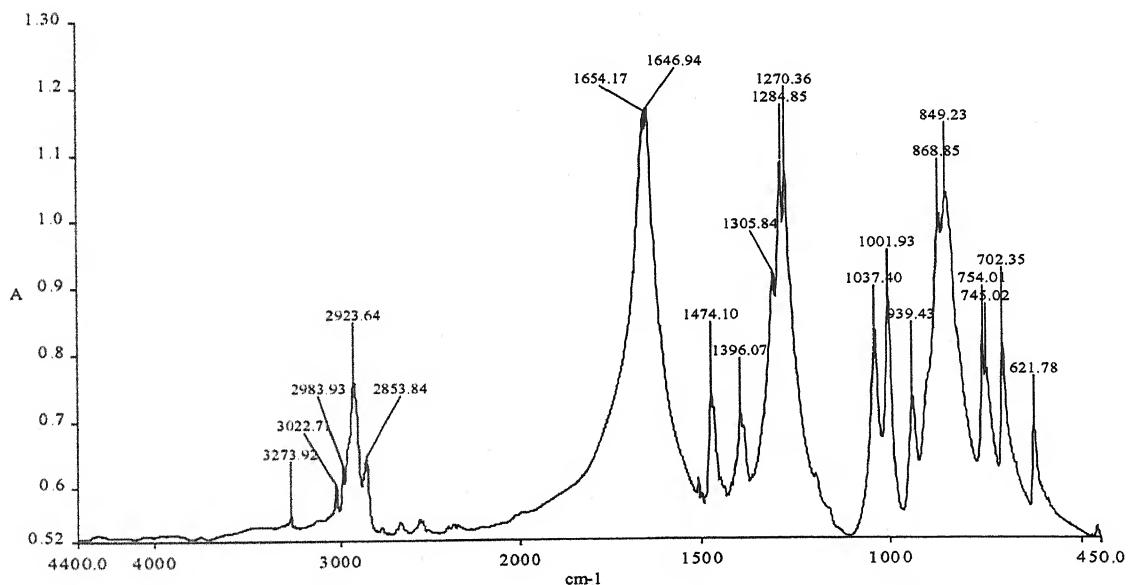
Fig.h.6 Spectrum of Drug Sample

7. HUMAN BOMB:
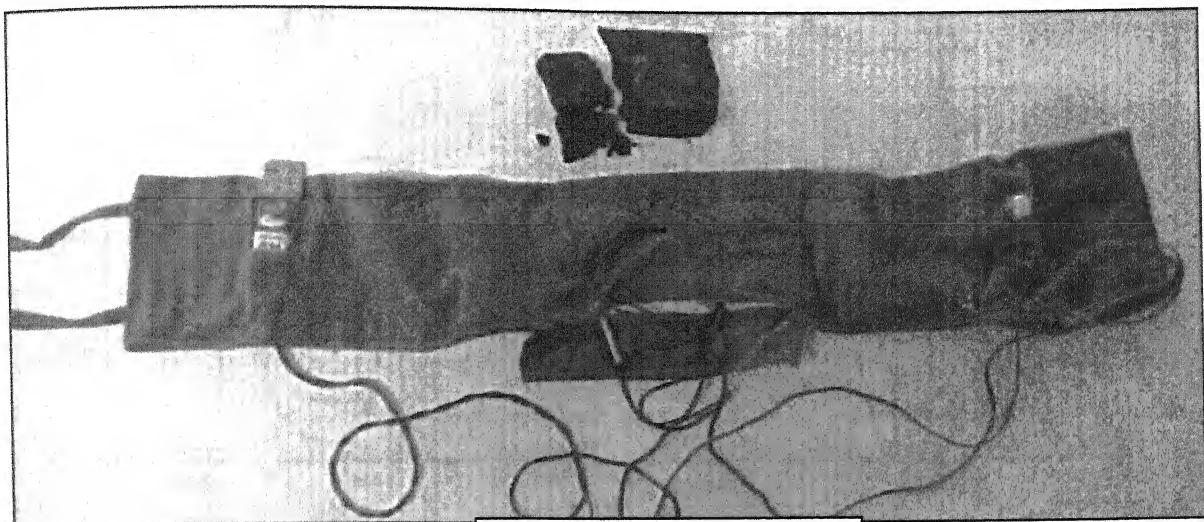
Human Bomb Belt

Generally human bombs use to hide explosive in their person in the form of a pouch or belt. In this case also, a broad cloth belt was used to tie around the waist. The belt had four segments, out of which one was fitted with on/off switch and batteries and other three were filled with black putty like material. Spectroscopic analysis of the material used to fill the belt produced a spectrum as given in fig.h-7. Pattern of absorption bands produced by the material gave a perfect library match with explosive substance RDX. Bands at 2923 cm^{-1} and 2853 cm^{-1} are indicative of a substance of petroleum origin. Thus, in this case also, mere FT-IR spectrum of the sample could correctly characterise RDX in the mixture filled in the belt of human bomb.
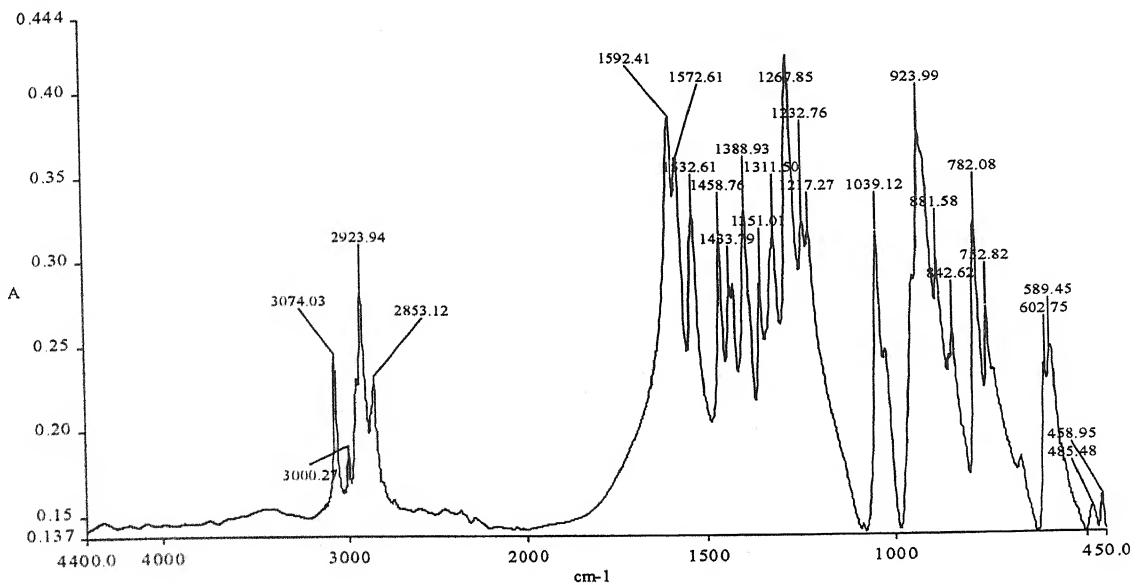
Fig.h.7 Spectrum of belt material

8. BOMBAY BOMB BLAST
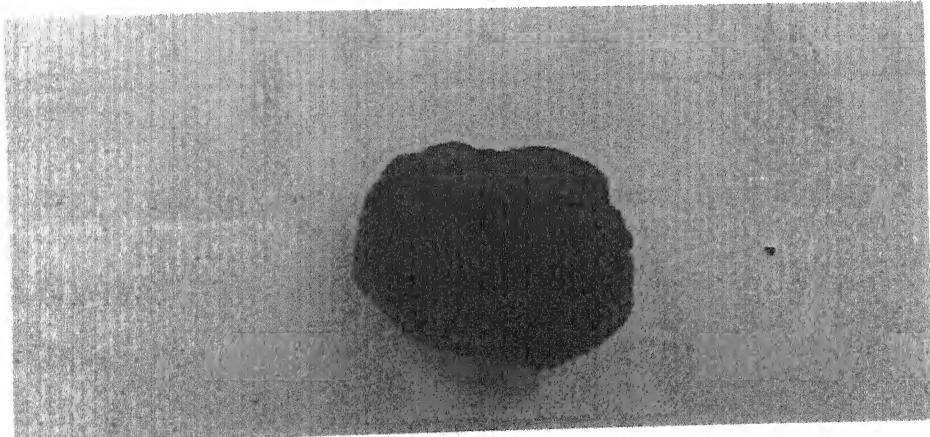
Black Explosive Material

In the Year 1993, there was a series of bomb blasts in the Bombay, commercial capital of India. In these blasts scooters were also used as Improvised Explosive Devices. Explosive formulation kept in the dickey of a scooter on spectroscopic analysis produced a spectrum as given in fig.h-8. Pattern of absorption bands (cm^{-1}) at 3073, 1592,1575, 1458, 1432, 1422,

1388,1350, 1311, 1268 ,1233 1217, 1039, 1018, 925, 881, 842, 781, 753, 630, and 589   produced a library match of explosive substance RDX. Bands at 2923 cm^{-1} and 2852 cm^{-1} are indicative of a substance of petroleum origin. In this case, the spectrum confirmed the presence of RDX alongwith a substance of petroleum origin used as a moulding and shaping agent.
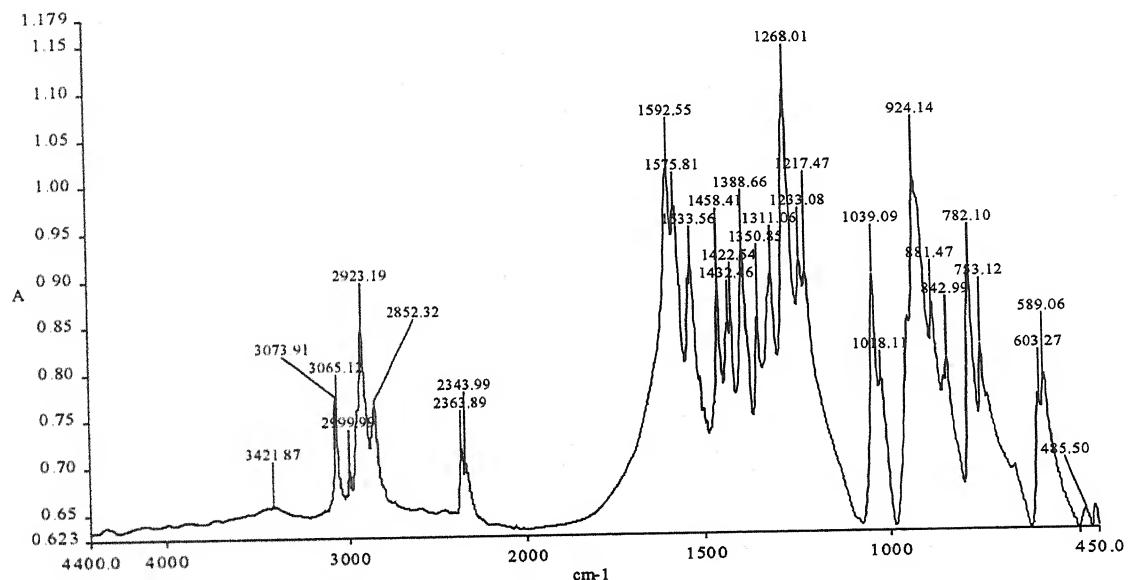
Fig.h.8 Spectrum of explosive material seized from dickey

9. YELLOW STONES
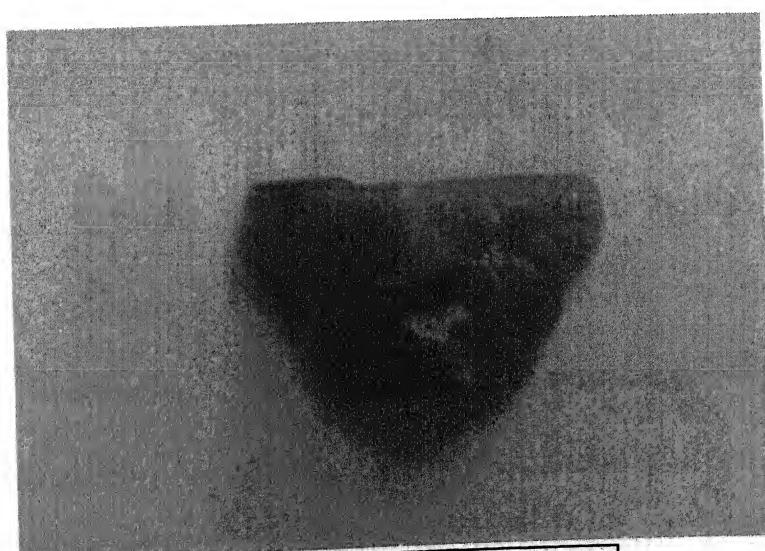
Explosive in the form of stone

In this case, some small pieces of yellow coloured stone like material were received from a very premier institute of India. The sample was referred to know the presence of any explosive substance in yellow stones. Spectrum (Fig.h-9) of this substance gave perfect match with TNT. No other characteristic band of any of the material of plant/animal/petroleum origin mixed with TNT could be observed in the spectrum.
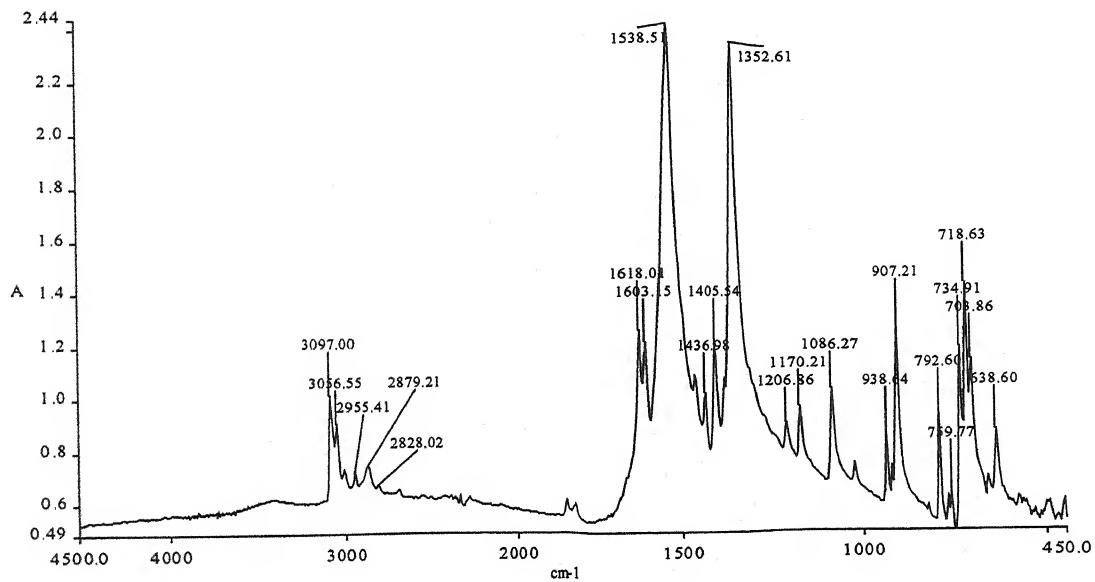
Fig.h.9 Spectrum of Yellow Stone

10. TRUCK STEPNEY

About 25 Kg. of explosive material was kept in the Stepney of a truck. The other components of the IED were also packed in the same compartment. The motive of the terrorists was to blow out a large building and cause damage to the life of several people. Material recovered from the Stepney was received for its analysis in the laboratory. FTIR analysis

revealed that the explosive used was RDX (Fig.h-10). It also gave characteristic bands for the presence of oil of petroleum origin.
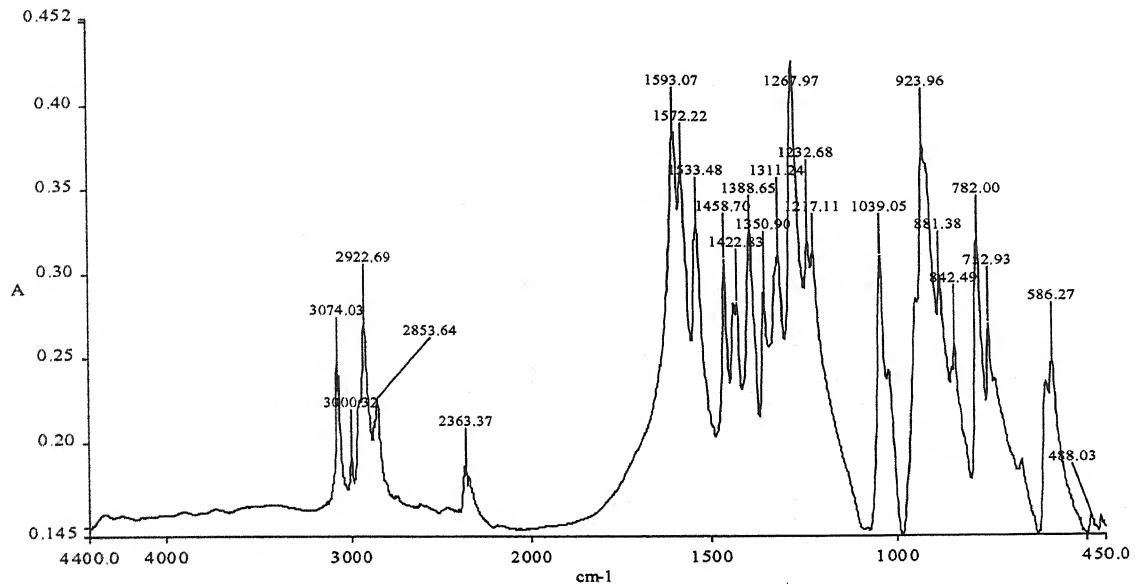
Fig.h-10 Spectrum of explosive material

11. CHIEF MINISTER'S ASSASSINATION

Explosive material scrapped from cardboard
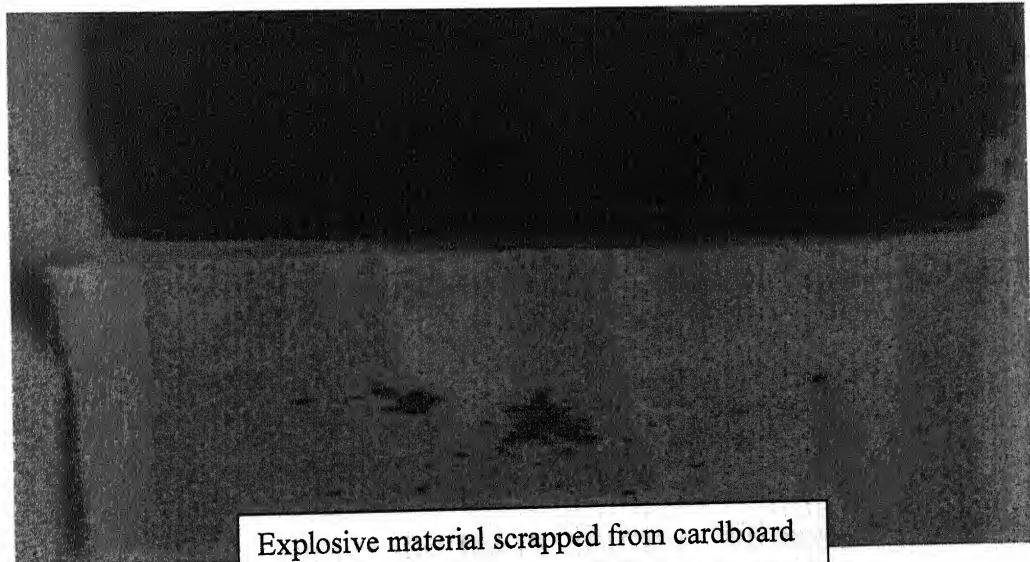
Former Chief Minister of a northern state of India was assassinated by a human bomb. Empty packets storing explosive material were recovered from the dust bins of the hide out of militants. Trace particles of black

coloured material adhering to the packets were scrapped off, and analysed by FTIR spectrophotometer. Pattern of absorption bands (Fig.h-11) produced by the material gave a perfect library match for explosive substance RDX. Bands at 2923 cm^{-1} and 2853 cm^{-1} are indicative of a substance of petroleum origin. Thus, in this case also, FT-IR spectrum of the sample could correctly characterise RDX in spite of being in small amount (mgs.)
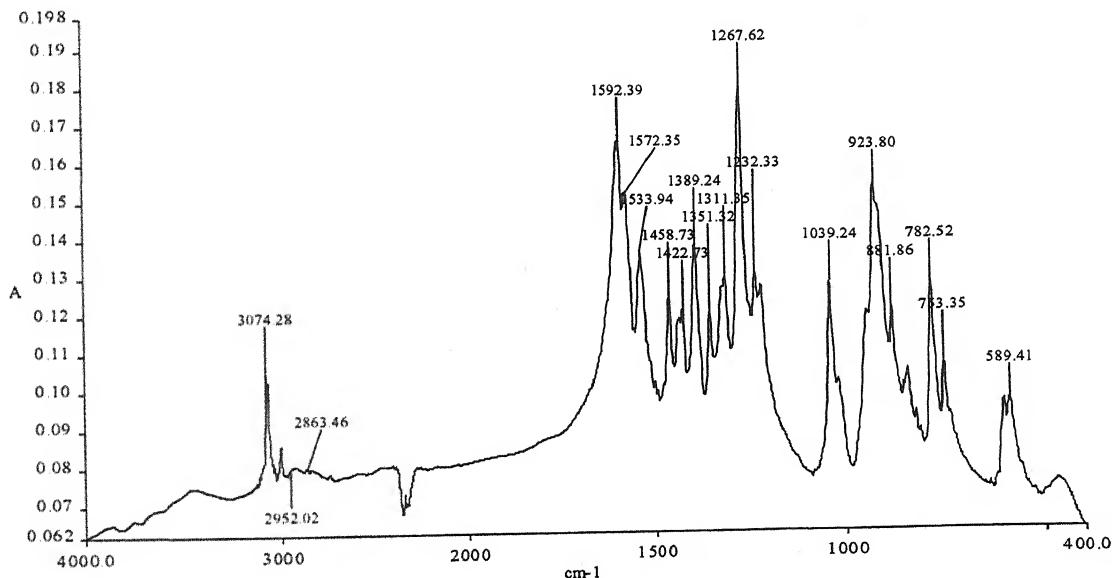
Fig.h-11Spectrum of scrapped material

12. SOIL LIKE POWDER

National Bomb Data Centre of National Security Guard sent a sample of soil like coarse powder for its analysis. The sample resembled with Shakker or brown sugar. Spectrum of this substance was recorded with the help of FTIR spectrophotometer. It gave all the bands characteristics to

TNT (Fig.h-12).   Hence the substance could easily be identified by the technique to be TNT.
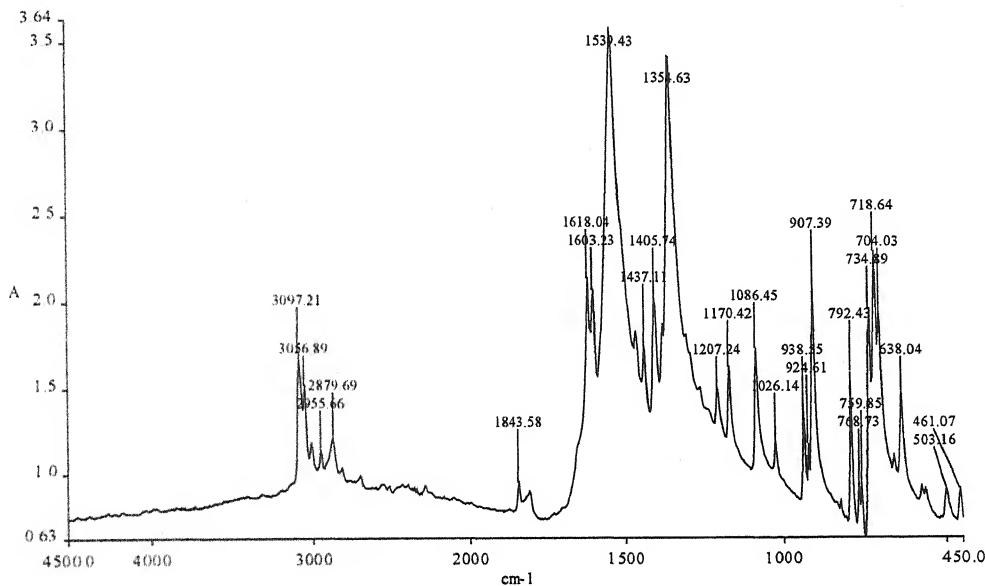
Fig.h-12 Spectrum of soil like coarse powder

POST BLAST CASES

Exhibits of cases pertaining to twin blasts occurred in 2003 in one of the most populated city of the country were chosen for the study under reference.   The samples were forwarded by National Security Guard, a prestigious investigating agency of the country.   Direct extraction of these exhibits with acetone was used for preliminary study for detection of likely type of explosive substance.   IR Spectrum was totally a mess containing numerous bands from which it was difficult to derive any information except that strong bands appeared in range 2900-3000 cm^{-1} to indicate –C-H stretching.   These samples on prior extraction with spectroscopic grade n-

pentane and subsequent extraction with acetone produced much better spectrum. Before preparing potassium bromide pellet complete evaporation of n-pentane and acetone was ensured by blowing hot air. Both spectra (fig.h.13 & h.14) matched with IR spectrum of RDX. Further absence of absorption band at 1746 cm^{-1} in the spectra of both extracts, direct with acetone and the other one with n-pentane followed by acetone indicated absence of vegetable/animal origin fat or oil.

In another case, colour tests and Thin Layer Chromatographic (TLC) analysis of samples of extracts of soil samples from craters formed by blasts indicated presence of organic explosive. TLC showed long streak without any reasonable interpretation. Spectrum of extract of crater soil (fig-h.15) was recorded using same methodology. On thorough scrutiny, it was found that spectrum is containing many absorption bands representing RDX. However, peculiar bands at 705 cm^{-1}, 722 cm^{-1}, 736 cm^{-1}, 911 cm^{-1} and 1459 cm^{-1} belong to TNT. IR spectra of the soil sample under reference indicated the presence of explosive material to be a mixture of RDX and TNT (fig.-h.16). Such a combination of TNT & RDX is used as military explosive cyclotol in which the ratio of RDX & TNT is 60:40. Another sample of RDX & TNT in ratio of 60:40 was prepared and its spectrum was recorded. Both spectra were studied side by side. Spectrum of standard RDX & TNT showed closer match to spectra of extracts of soil samples collected from craters (fig.-h.17 & fig.h17a). Results of the case sample under reference

were also studied and confirmed with GC-MS analysis. It showed two peaks in Total Ion Current Chromatogram (TIC) representing RDX and TNT. Further analysis of TIC showed mass ions 205, 148, 128, 120, 102, 75 & 46 representing RDX and mass ions 210, 193, 180, 164, 149, 143, 89, 76 & 46 belonging to TNT.

Thus IR spectrophotometric analysis, itself has been to produce enough data, which could identify two explosive substance RDX & TNT in soil samples of each crater formed due to blast of bombs.
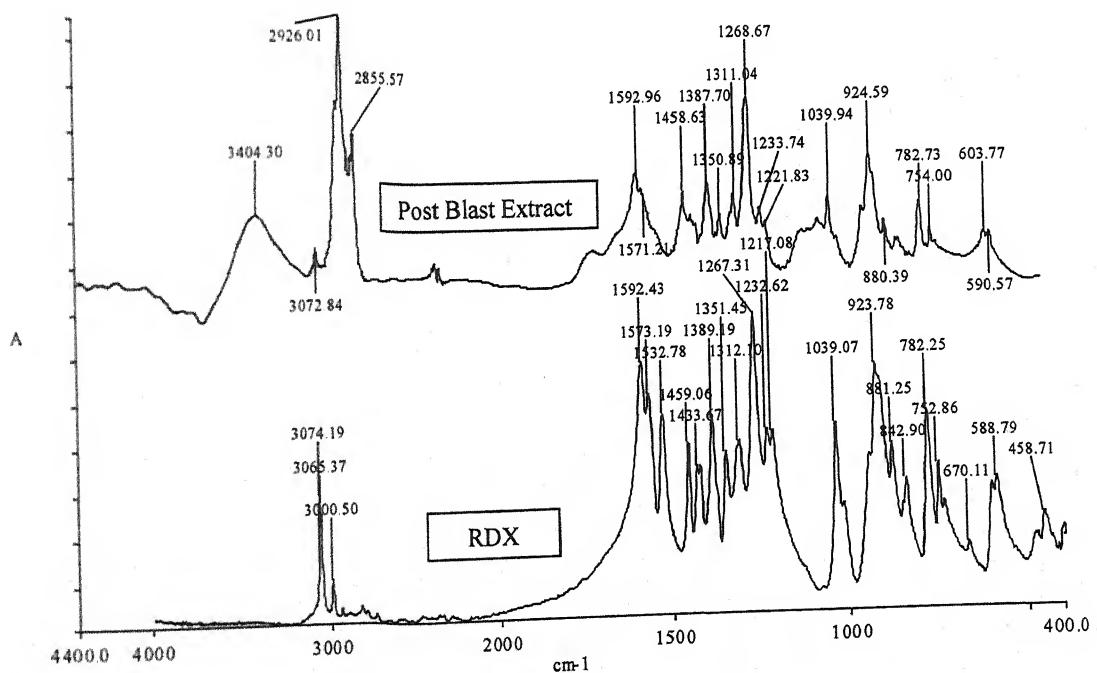
fig.h.13 Extract of post blast residues matching with RDX from site-1
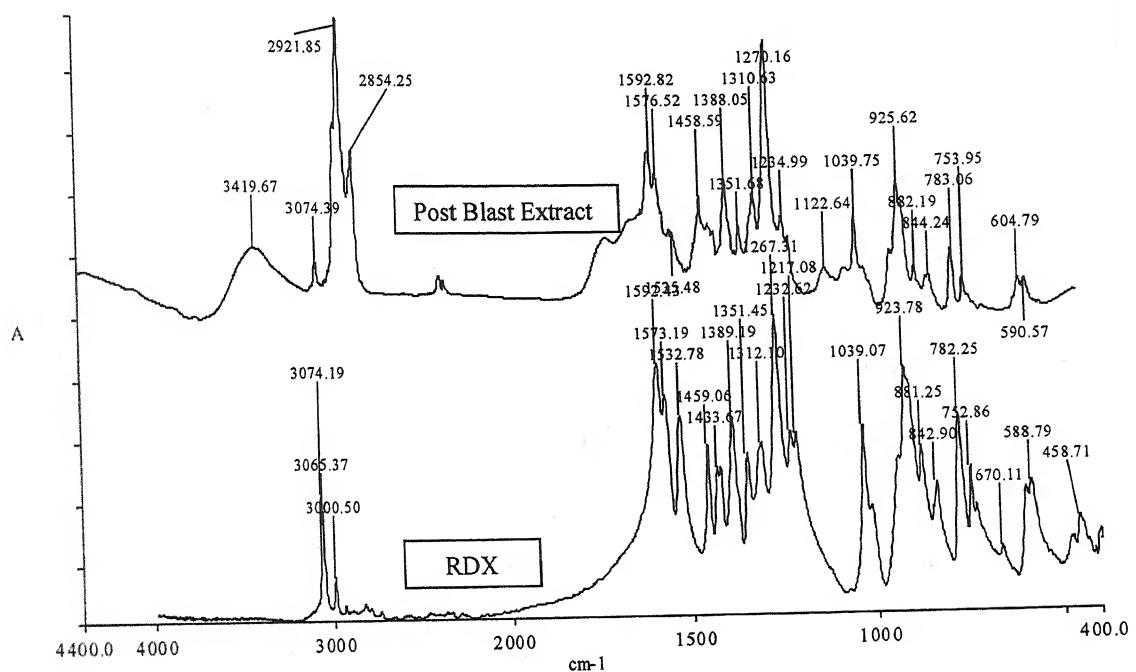
fig.h.14 Extract of post blast residues matching with RDX from site-2
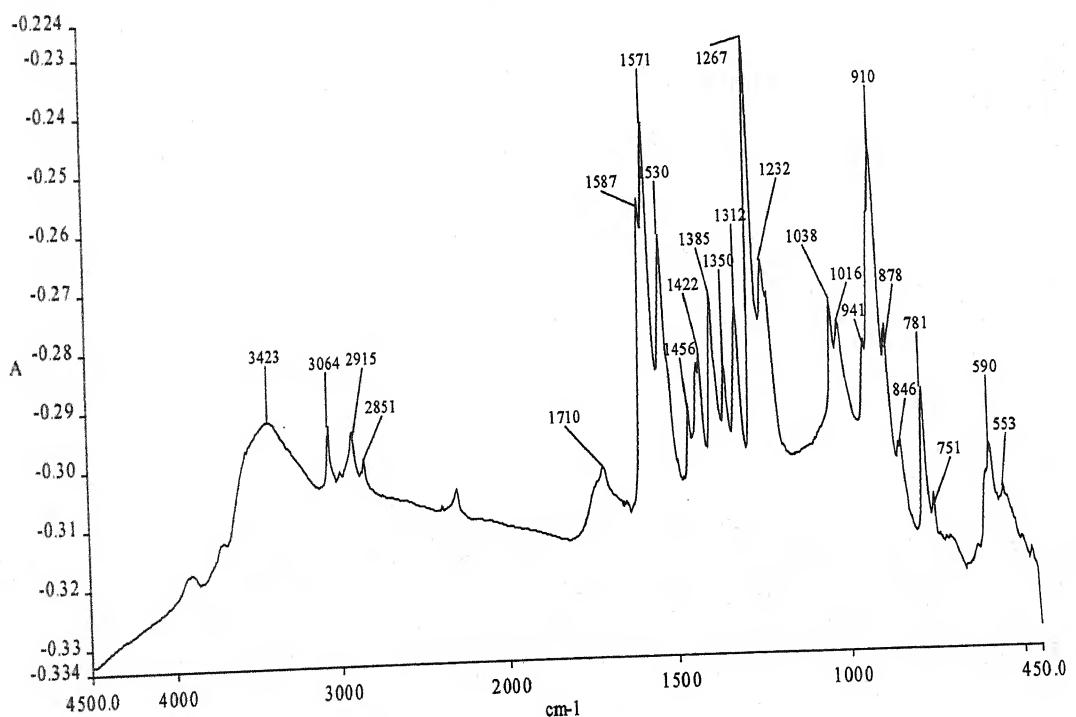
fig.-h.15 Extract of post blast residues from crater
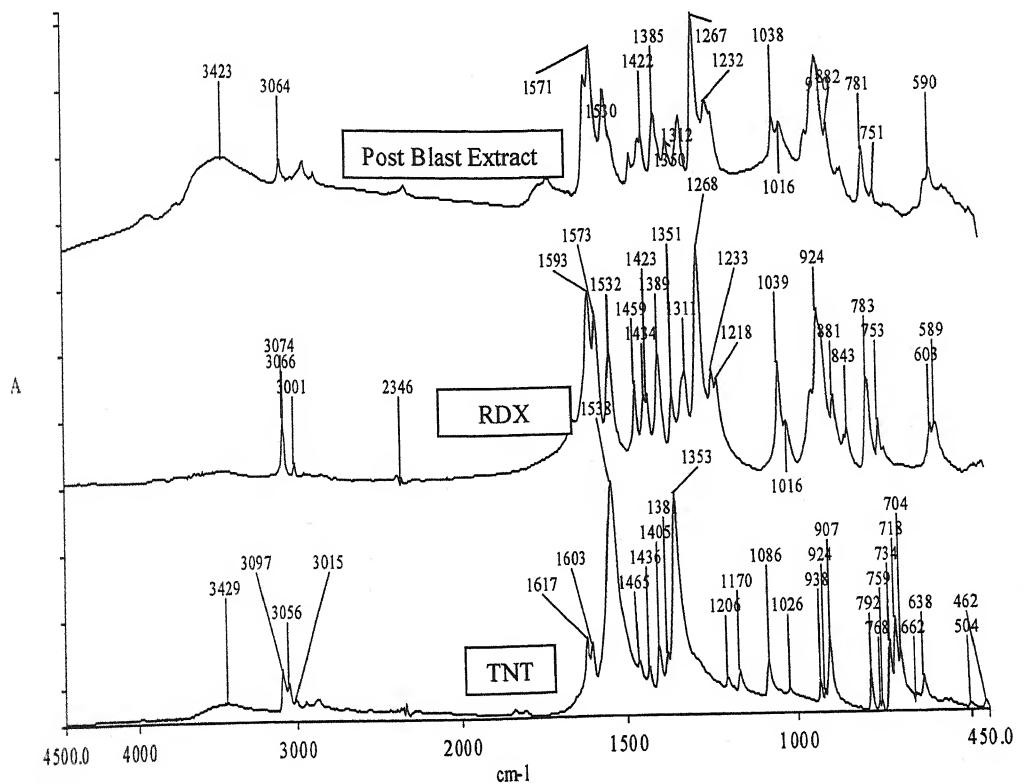
fig.-h.16 Extract of post blast residues of crater matching with RDX & TNT
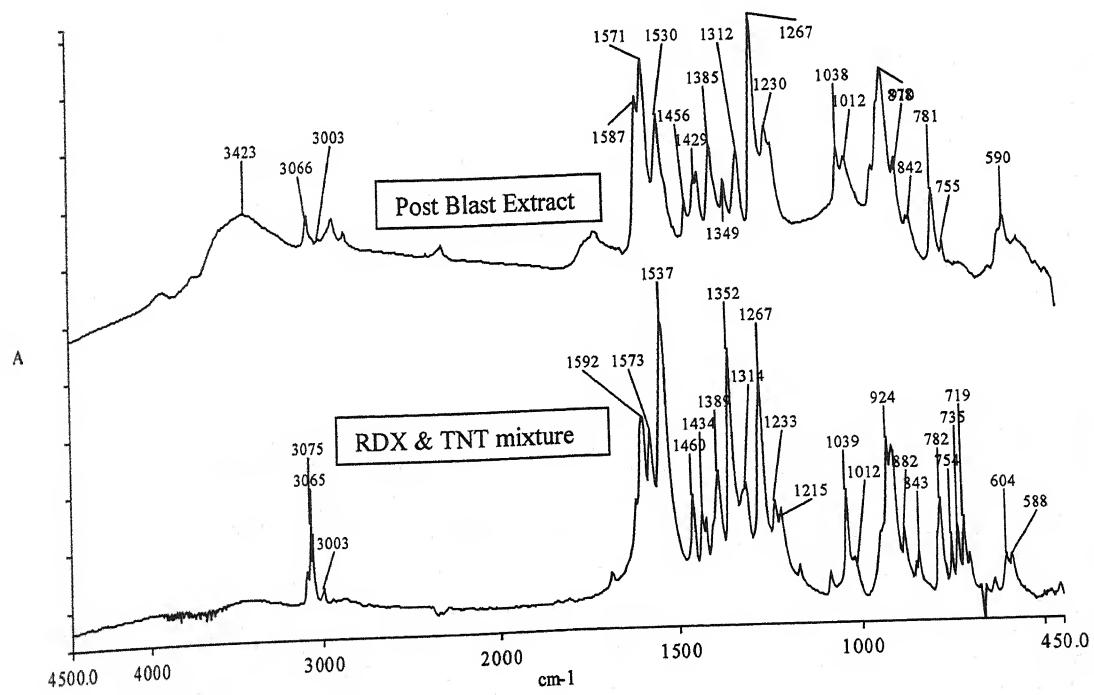
fig.-h.17 Extract of post blast residues of crater matching with RDX & TNT mixture
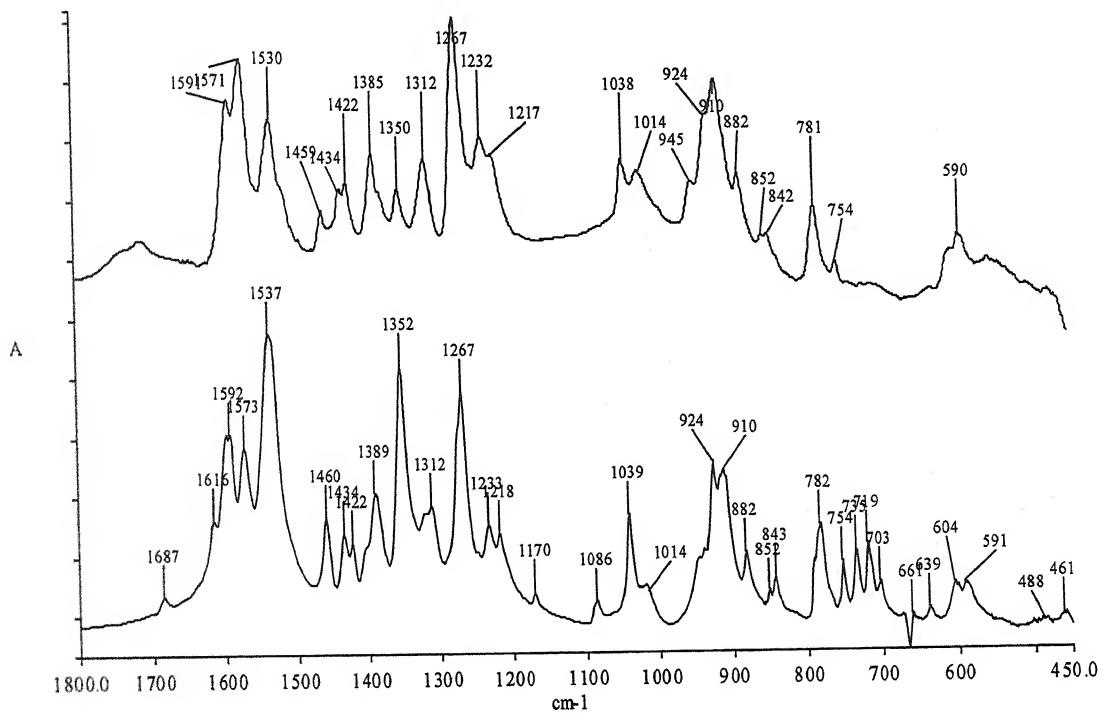
Fig.h17a Extract of post blast residues of crater matching with RDX & TNT mixture with expanded x-axis

Chapter-6

Summary

The forensic analysis of explosives deals with the identification of explosive substances recovered in large quantities, traces and also in post blast samples. The analytical results may give the direction to a police investigation whether the explosion is intentionally caused or an accidental one. If intentional, whether is it a criminal, a political or a terrorist act? Is there a link to an earlier occurrence? Is there sufficient evidence to frame charges against the suspect?

There are a variety of explosive substances used by the terrorists or explomanics, however, the most frequently encountered explosives are TNT, CE, PETN, RDX and Nitroglycerine to some extent. This thesis is mainly concentrated on four explosives namely TNT, CE, PETN and RDX. These explosives are representative of two very important classes of explosives i.e. nitramines and nitro esters.

A wide range of methods has been used for the identification of unexploded explosives and for post blast residues. A review of such techniques is presented in second chapter. Colour tests can easily be performed even by a person with a little training. Although, the main disadvantage of colour tests for identification of explosive substances lies in their less reliability. Yet, colour tests are extensively used as presumptive

tests in many forensic and other explosive analyzing laboratories. Thin layer Chromatography (TLC) has the advantages of being simple, rapid, inexpensive and relatively sensitive. However, the combination of Rf values and colours produced by chromogenic spraying reagents used for detection are not considered sufficient for identification of explosive compounds. Gas Chromatography is a highly acclaimed technique in analytical chemistry. However, the compatibility of GC with the analysis of explosives like nitrate esters and nitramines is not very good. Thermal Energy Analyser (TEA) is a useful detector for gas chromatograph and liquid chromatograph but it gives only an indirect inference regarding explosive substances. High Performance Liquid Chromatography is a suitable technique for the analysis of thermally labile compounds including explosives. To get separation in an explosive formulation by Liquid Chromatography is not an easy job for an analyst. Mass Spectrometry is a very sensitive technique for detection and identification of any organic explosive substance. Hyphenation of mass spectrometer with other separation devices like Gas Chromatograph and Liquid Chromatograph enhances its usefulness. To get useful results, one has to introduce the formulation in the solution form into the instrument, which always leaves trace contaminants in the instrument. **Infra Red spectrophotometric methods were found quick, easy to perform, reliable and compound specific. Moreover sampling techniques involve**

mere preparation of a pellet, which nowhere contaminates the instrument.

In third chapter the details of the instrument and various materials used in the study have been elaborated. Perkin Elmer make FT-IR spectrophotometer model 1605 with resolution of 4 cm^{-1} has been used in the study. Polystyrene film was used to calibrate the instrument. Substances of petroleum, vegetable, animal, sugar and starch origin have been studied. The nature of explosive substance used in the study has also been described in detail. For recording of FTIR spectra, potassium bromide pellet technique with "*mini hand held sampling press*" was found more useful. For the preparation of a pellet, 1 mg of explosive substance was mixed with about 100 milligram of potassium bromide and ground thoroughly. In liquid samples, a thin layer of liquid was spread on a pure potassium bromide pellet to record the spectrum. In the case of post blast analysis, the residues were washed with n-pentane and then extracted with acetone. Thereafter, solvent was evaporated by blowing nitrogen gas and spectra were recorded.

In fourth chapter various results obtained by the analysis of samples were discussed in detail. Spectra of eleven products of petroleum origin were evaluated and found that **it was not possible to distinguish among all the eleven petroleum product substances individually based on their infrared spectra.**

Spectra of substances of vegetable origin have also been discussed in detail. It was found that **infrared spectrum of vegetable oils also did not indicate characteristic peaks to distinguish among one another except in the case of castor oil.**

Spectra of substances of animal origin i.e. **Lard and Milk Fat were found similar to that of the spectra of vegetable oils with respect to strong absorption bands.**

Spectra of sugars and starches were found to contain broad bands. **Individualisation among these products was not possible on the basis of their spectra.**

A number of characteristic bands were found in the spectra of explosive substances. On the basis of IR spectra, **Individualisation of each of the explosive substance used in the study was possible.**

Spectra of explosives mixed with various substances of animal, petroleum and vegetable origin and wax, fat, starches and sugars in the form of mixtures were discussed. It was observed that **detection of explosives by the method of spectroscopy in these mixtures was possible. In spite of the fact that sugars and starches produce many absorption bands, which mask or obscure the peaks of explosive substances, still identification of explosive substance was possible. The spectra of mixtures gave fair indication of additives like oils of petroleum and animal origin, wax, and fat.**

The explosive substance down to 50% level in presence of various moulding agents used in this study could be detected from the numerous strong and weak absorption bands linking to its structure. Even the library search in spectra of such mixtures could provide maximum probability of the match with the correct identification of the explosive substance. **The main emphasis was given on the correct identification of explosive substance within minimum possible time.**

In fifth chapter about a dozen samples received in explosive Division of Central Forensic Science Laboratory, Chandigarh, were analysed by IR spectrophotometric method. **Active explosive used in these samples were identified on the basis of IR analysis.**

Even some samples of post blast residues of explosions of national concern were also studied. In two blasts occurred in year 2003 in a metropolitan city, RDX could be detected by cleaning post blast residues with n-pentane, then extraction with acetone and making pallet with potassium bromide with a residue left on evaporation. Similarly, more than one explosive substance could be easily identified in unexploded formulations as well as in post blast residues.

Chapter-7

CONCLUSIONS

1. Experiments have shown that FT-IR Spectrophotometry looks quite reasonable, quick and successful technique for the identification of commonly used organic explosive substances including indication of moulding agents in the improvised formulations.

2. Moulding agents form just a small part of the whole of the improvised organic explosive formulation. Petroleum products used for their moulding in improvised formulations of explosive substances are indicated by asymmetric and symmetric stretching absorption bands due to repeated methylene groups forming chains in hydrocarbons. Very strong absorption bands are produced in range from 2800-3000 cm^{-1} of electromagnetic region for these substances.

3. Oils and fats of plant and animal origin contain triglycerides-esters of fatty acids comprising long chains of repeated methylene groups. Absorption peaks indicating asymmetric and symmetric stretching vibrations appear in their spectra as usual in range of 2800-3000 cm^{-1} as in the case of petroleum products. However, in this region of spectrum also appears a peak at about 2924 cm^{-1} representing carbon hydrogen stretching attached to carbon – carbon double bond. In addition, a group of characteristic absorption bands in the range from

1100 cm^{-1} to 1250 cm^{-1} (triplet with maxima in between 1160 to 1170 cm^{-1}) and absorption peak representing carbonyl stretching in 1735-1750 cm^{-1}, also appear. In the case of spectra of mixtures of explosive substances with the oils and fats of vegetable and animal origin, absorption peak due to carbonyl group appears in a region with no absorption peak due to any of the four explosive substances undertaken for this study. Presence of typical strong absorption peak due to carbonyl group, in the spectrum also distinguishes the oil in the mixtures to be of vegetable & animal origin rather than that of petroleum origin.

4. In the mixtures of explosive substances with oils combined with starches or sugars to form dough, again, identification of the explosive material by Infrared Spectrophotometry is possible. It is due to the fact that explosive substances form major component of the mixtures. On the other hand, most of the absorption bands produced by oils, sugars and starches appear with much reduced intensity in the spectra due to their low concentration in the formulations. Starches and sugars, being complex organic molecules, produce plenty of absorption bands in their spectra in the range from 400 cm^{-1} to 4000 cm^{-1}.

5. Mostly in improvised organic explosive formulations confiscated in criminal cases, oils of petroleum origin have been detected. These

oils in pure state produce spectra with a few strong absorption bands in the mid infrared range. In a concentration of about 10-15 % quantity in the mixture enough for moulding or shaping, only a few strong absorption bands in range 2800-3000 cm^{-1} remain predominant. Remaining whole of the spectrum range from $400cm^{-1}$ to 2800 cm^{-1} is quite free from absorption bands representing petroleum products. Interestingly, plenty of absorption peaks representing molecular structure of explosive substances appear in the range below 1500 cm^{-1}. On the other hand petroleum products do not produce significant strong absorption bands in this range due to their inherent nature and being in a low concentration in the mixtures.

6. FT-IR Spectrophotometry has a great potential in correct identification of organic explosive substances in improvised formulations, which can provide quick information to the law enforcement agencies. Thus, the tool should be invariably used by forensic scientists for getting quick secure proof of improvised organic explosive formulation involved in criminal activities, even if the explosive substances TNT, CE, PETN and RDX, have been camouflaged or disguised to imitate Indian sweets or something else.

7. In the case of post blast analysis, apparent weakness of technique of requirement of pure sample in enough quantity does not stand anywhere. Proper extraction method for eliminating extraneous

soluble impurities is required to be followed. It has also a potential to indicate moulding agent of petroleum, vegetable or animal origin in addition to identification of explosive substance.

8. It can also provide fairly correct information of explosive substance comprising mixtures of organic explosive substances both in unexploded formulations as well as in post blast samples. Capability has been amply demonstrated by detecting RDX and TNT in case of soil collected from craters of about more than half dozen chain blasts. If the requirement of amount of substance/solution required for sophisticated techniques like GC, GC-MS, LC and LC-MS etc., is compared with IR spectrophotometer, it does not lag behind on this aspect also. It is due to the fact that for all these techniques, to prepare a solution of the suspect sample for injection into the instrument, a certain minimum amount of sample is required. It needs to be filtered and concentrated also. A minimum amount of solution is also required to fill the vial of the auto sampler or for repeated injections into the instrument in case syringe injection. On the other hand, FT- IR Spectrophotometry is a non-destructive technique where explosive substance can be recovered with solvent extraction for further analysis. IR Spectrophotometry is very convenient for thermo labile explosive substances, another advantage over GC or other

techniques hyphenated to GC, where the explosive substance breaks down in the column due to heat of Gas Chromatograph.

9. Hence, FT-IR Spectrophotometry can form a routine analytical technique for quick analysis of organic explosive substances in formulation and in post blast residues. Even a mixture comprising more than one organic explosive substance can also be analysed correctly in both unexploded and post blast residues. It is also possible to get reasonable information of moulding agents used in improvised organic explosive formulations. Furthermore the technique is non-destructive in nature. It allows easy extraction of explosive substance from Potassium Bromide pellet for any other analysis.

In nutshell, after conducting hundreds of analyses of simulated organic samples, case exhibits of unexploded improvised formulations & post blast residues, it has been found that FT-IR Spectrophotometry has met the requirement of quickness and correctness, the main virtue of any forensic tool.

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GLOSSARY

S.No.	Term	Definition of Term
1.	API	Atmospheric Pressure Ionisation
2.	APCI	Atmospheric Pressure Chemical Ionisation
3.	CAD	Collision Activated Dissociation
4.	CE	Composition Exploding or 2,4,6-trinitrophenylmethylnitramine
5.	CID	Collision Induced Dissociation
6.	CIMS	Chemical Ionisation Mass Spectrometry
7.	Cyclotol	TNT & RDX mixed explosive
8.	C-18,RP-18,LC-18 etc.	Octadecylsilane
9.	DNT	Dinitrotoluene
10.	DC	Direct-current
11.	EC	Electrochemical
12.	ECD	Electron Capture Detector
13.	EGDN	Ethylene Glycol Dinitrate
14.	EGMN	Ethylene Glycol Mononitrate
15.	EI	Electron Ionisation
16.	EIMS	Electron Ionisation Mass Spectrometry
17.	ESI	Electro Spray Ionisation

S.No.	Term	Definition of Term
18.	FTIR	Fourier Transform Infra Red (Spectrophotometer)
19.	GC	Gas Chromatograph
20.	GC-CIMS	Gas Chromatograph- Chemical Ionisation Mass Spectrometer
21.	GC-EIMS	Gas Chromatograph- Electron Ionisation Mass Spectrometer
22.	GC-MS	Gas Chromatograph-Mass Spectrometer
23.	GC-NCIMS	Gas Chromatograph- Negative Chemical Ionisation Mass Spectrometer
24.	GC-PCIMS	Gas Chromatograph- Positive Chemical Ionisation Mass Spectrometer
25.	HPLC	High Performance Liquid Chromatograph
26.	HPLC-API-MS	High Performance Liquid Chromatograph- Atmospheric Pressure Ionisation- Mass Spectrometer
27.	HPLC-NCI	High Performance Liquid Chromatograph- Negative Chemical Ionisation
28.	HPLC-PCI	High Performance Liquid Chromatograph- Positive Chemical Ionisation
29.	HTGC-MS	High Temperature Gas Chromatograph-Mass Spectrometer
30.	I. D.	Internal Diameter
31.	IMS	Ion Mobility Spectrometer

S.No.	Term	Definition of Term
32.	LC	Liquid Chromatograph
33.	LC-CN	Cyanoalkyle
34.	LC-TSP	Liquid Chromatograph-Thermospray
35.	m	Meter
36.	mm	Millimeter
37.	M^+	Molecular Ion
38.	MH^+	Hydrated Molecular Ion
39.	MNT	Mononitrotoluene
40.	MS	Mass Spectrometer
41.	m/z	Mass to charge ratio
42.	NG	Nitro Glycerin or Nitroglycerine
43.	Ng	Nanogram
44.	NCI	Negative Chemical Ionisation
45.	NICI	Negative Ion Chemical Ionisation
46.	Pg. or pg	Picogram
47.	PCI	Positive Chemical Ionisation
48.	PETN	Pentaerythritol Tetranitrate
49.	PICI	Positive Ion Chemical Ionisation
50.	ppb	Parts per billion
51.	RF	Radiofrequency